Aerojet Propulsion Division

# Preparation and Characterization of Dense, Cryogenic, Gelled, Heterogeneous Oxidizers

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Prepared For:
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**GenCorp**

**AEROJET**

Contract NAS 3-25822

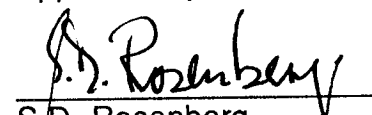# PREPARATION AND CHARACTERIZATION OF DENSE, CRYOGENIC, GELLED, HETEROGENEOUS OXIDIZERS

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# FOREWORD

The NASA, Lewis Research Center, Project Manager for this program was Ms. Diane Linne. The Program Manager at Aerojet Propulsion Division was Dr. S.D. Rosenberg. Mr. R.E. Anderson was the Project Engineer and Principal Investigator on the program. The research was performed in the Engineering Laboratories of the Aerojet Propulsion Division, Test and Laboratory Operations, and was managed by Dr. E.M. Vander Wall. Mr. R.K. Schaplowsky, Manager of the Engineering R & D Laboratories, supervised the research. Mr. J.A. Cabeal built up the special test apparatus/equipment required for the research and performed the major part of the experiments and gel characterizations. Mr. R.E. Anderson analyzed and evaluated the experimental data and prepared the technical reports for the program.

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# I. INTRODUCTION

## A. BACKGROUND

Dense, cryogenic, gelled, heterogeneous oxidizers are a new class of high energy density liquid propellants which were probably first conceived in early 1988[1]. This class of oxidizers provides much higher theoretical density impulses with common rocket fuels than are presently available. The use of these oxidizers with common rocket fuels such as RP-1 (kerosene), Aerozine-50 (50 %wt hydrazine and 50 % wt unsym-dimethylhydrazine), etc., yields density impulses up to about 20 % greater than is possible with $LO_2$/RP-1. When used with a nonmetallized, heterogeneous fuel, such as RP-1 plus solid carbon, they provide a density impulse 27 % greater than that of $LO_2$/RP-1.

Such oxidizers are comprised of at least three components, namely: (1) a high-energy, cryogenic, liquid oxidizer, (2) a very dense, fine particulate, energetic oxidizer which is solid at the storage temperature of the cryogen and is chemically compatible with and insoluble in the cryogen, and (3) a gelling agent which will gel the cryogen and keep the dense solid particulate oxidizer uniformly dispersed in the cryogen. A preferred example of the first component, the cryogenic liquid-carrier oxidizer, is liquid oxygen because of its low cost, minor environmental impact, high performance with common fuels, and advanced state of operational use in liquid rockets. Preferred examples of the second component, the very dense oxidizers which are solids at the operating temperature of the cryogenic carrier, include the normally-liquid oxidizers, nitrogen tetroxide ($N_2O_4$), maximum density fuming nitric acid (MDFNA, 56 % wt $HNO_3$/44 % wt $N_2O_4$), and hydrogen peroxide ($H_2O_2$). Preferred examples of the gelling agents for the cryogenic liquid carrier include ultra-fine particles of the normally-liquid dense solid oxidizer ($N_2O_4$, MDFNA, or $H_2O_2$) and ultra-fine silica. A typical dense, cryogenic, gelled, heterogeneous oxidizer can contain up to approximately 60 % volume of solid phase oxidizer and typically requires 2 to 3 % volume gelling agent to maintain a uniform gelled dispersion of the solid in the cryogenic carrier.

The very high densities of the normally-liquid oxidizers, $N_2O_4$ and $H_2O_2$, when frozen and chilled to cryogenic temperatures are demonstrated in Figures 1 and 2. Solid $N_2O_4$ and $H_2O_2$ at the normal boiling point of oxygen (90.18 K, -297.35 °F) are approximately 38 and 24 % more dense than their respective liquid phases at ambient temperature and about 73 and 58 % more dense than liquid oxygen itself. The theoretical specific impulses and density impulses of several propellant combinations based on this new class of cryogenic, heterogeneous, oxidizers are compared in Table I and Figure 3 with those of several current standard liquid propellants and with some advanced, cryogenic, high-energy metallized propellants.

The new class of dense, cryogenic, gelled, heterogeneous, oxidizers is significant in two very important respects. First, their higher densities translate into major improvements in payloads in

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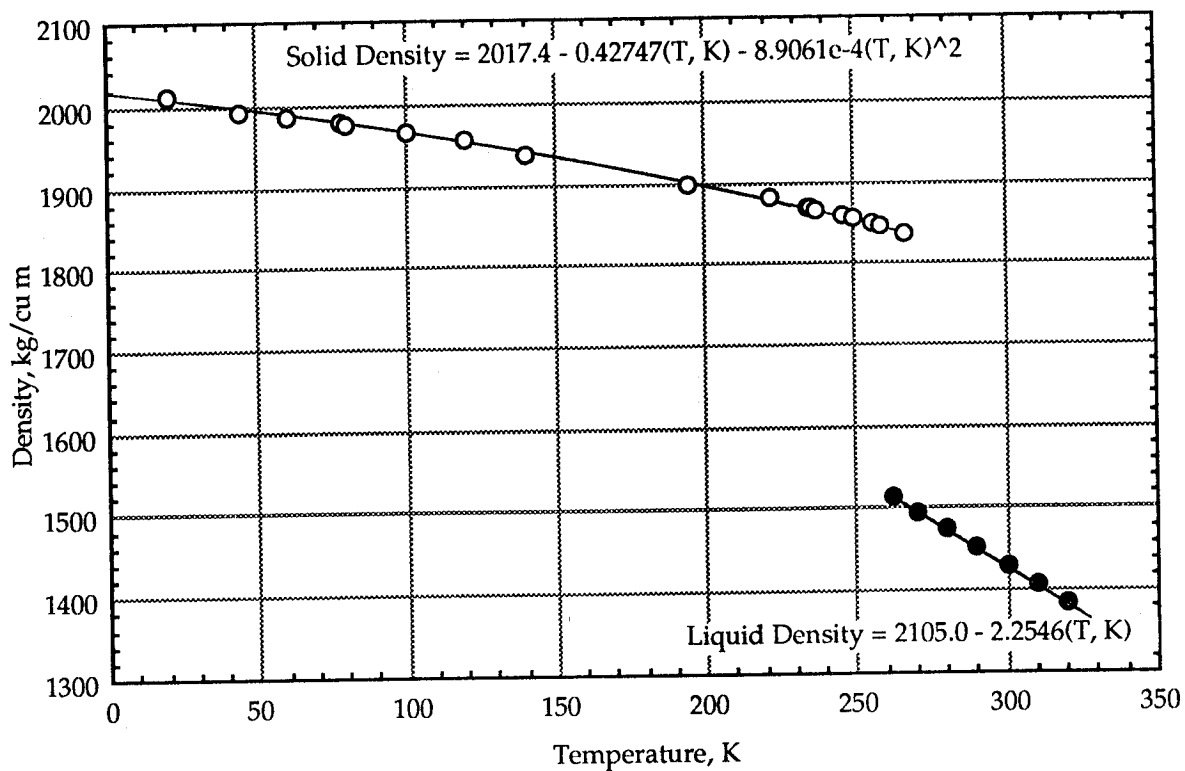
Figure 1. Density of Liquid and Solid Nitrogen Tetroxide
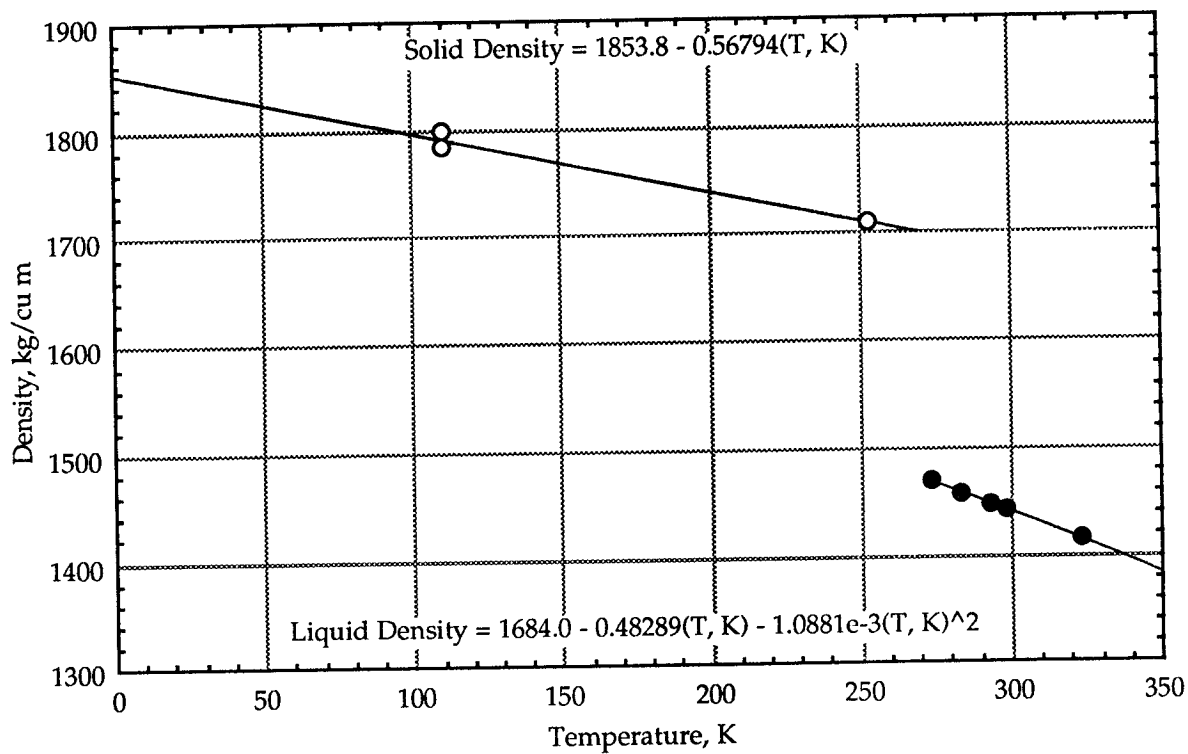


Figure 2. Density of Liquid and Solid Hydrogen Peroxide

Table I

Performance Characteristics of New, Advanced, and Current Liquid Propellants

| Propellant Combination | Mass Mixture Ratio, O/F | Bulk Density, kg/cu m [a] | Opt. S.L. Specific Impulse [b] | Density Impulse [c] |
|---|---|---|---|---|
| **Propellants Based on New Class of Cryogenic Heterogeneous Oxidizers [d]** | | | | |
| LO2 + N2O4(s)/Aerozine-50 | 1.80 | 1229 | 295.6 | 363.4 |
| LO2 + N2O4(s)/RP-1 | 3.60 | 1285 | 283.1 | 363.8 |
| LO2 + H2O2(s)/RP-1 | 4.60 | 1278 | 284.2 | 363.3 |
| LO2 + H2O2(s)/RP-1 + C(s) (30/70 wt) | 3.80 | 1441 | 270.6 | 390.0 |
| **Advanced Cryogenic Metallized Propellants [e]** | | | | |
| LO2/ RP-1 + Al (35/65 wt) | 1.00 | 1286 | 281.6 | 362.3 |
| LO2/ RP-1 + Be (60/40 wt) | 1.40 | 1094 | 310.4 | 339.7 |
| **Current Standard Liquid Propellants** | | | | |
| LO2/RP-1 | 2.60 | 1020 | 300.2 | 306.3 |
| N2O4/Aerozine-50 | 2.00 | 1196 | 289.2 | 345.9 |

[a] Calculated using the following component densities: LO2 (NBP), 1.141; liquid N2O4, 1.433; solid N2O4, 1.95; solid H2O2, 1.80; RP-1, 0.800; Aerozine-50, 0.899; solid C, 1.9; Al, 2.70; Be, 1.85 g/cc

[b] Sea level specific impulse in units of "sec," for optimum expansion from 6.89 MPa (1000 psia) to 0.101 MPa (14.7 psia). 1 "sec." = 9.80665 N•s/kg

[c] Product of optimum sea level specific impulse (see footnote b) in unit of "sec." and propellant bulk density in unit of g/cc. 1 g/cc = 1000 kg/cu m

[d] The heterogeneous oxidizers and the heterogeneous fuel assumed to contain 50 % volume of solid N2O4, H2O2, and/or carbon (i.e., 63 % wt N2O4(s) in LO2, 61 % wt H2O2(s) in LO2, and 70 % wt carbon in RP-1)

[e] Metal loadings selected to maximize payload based on a fixed volume system analysis (Ref: Zurawski, R.L. and Green, J.M., "An Evaluation of Metallized Propellants Based on Vehicle Performance", NASA Tech. Memo. 100104, AIAA-871773, July, 1987). Propellant performance data taken from: Zurawski, R.L., "Current Evaluation of the Tripropellant Concept", NASA Technical Paper 2602, June, 1986
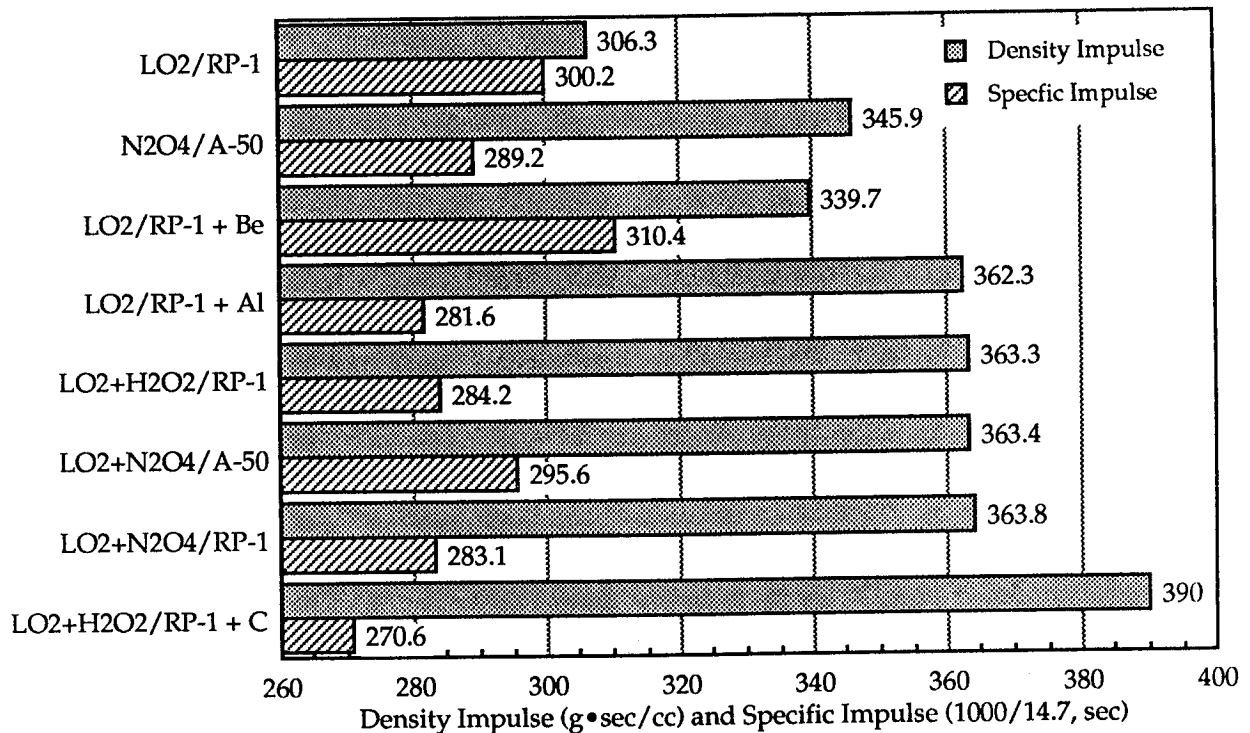


Figure 3. Performance Comparison of Current and Advanced Liquid Propellants

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volume limited applications, equaling or exceeding the gains possible with some of the best advanced metallized propellants. Second, they contain only relatively innocuous elements, (i.e., carbon, hydrogen, oxygen, and nitrogen) thereby, greatly reducing environmental impact and eliminating the problems associated with utilizing metals or halogens in rocket engines. Typical payload advantages are displayed in Figure 4 and are based on the same type of fixed-volume analysis utilized by Zurawski and Green[2] except that optimum sea level specific impulses (6.89/0.101 MPa, 1000/14.7 psia) were assumed rather than vacuum specific impulses at an area ratio of 60.
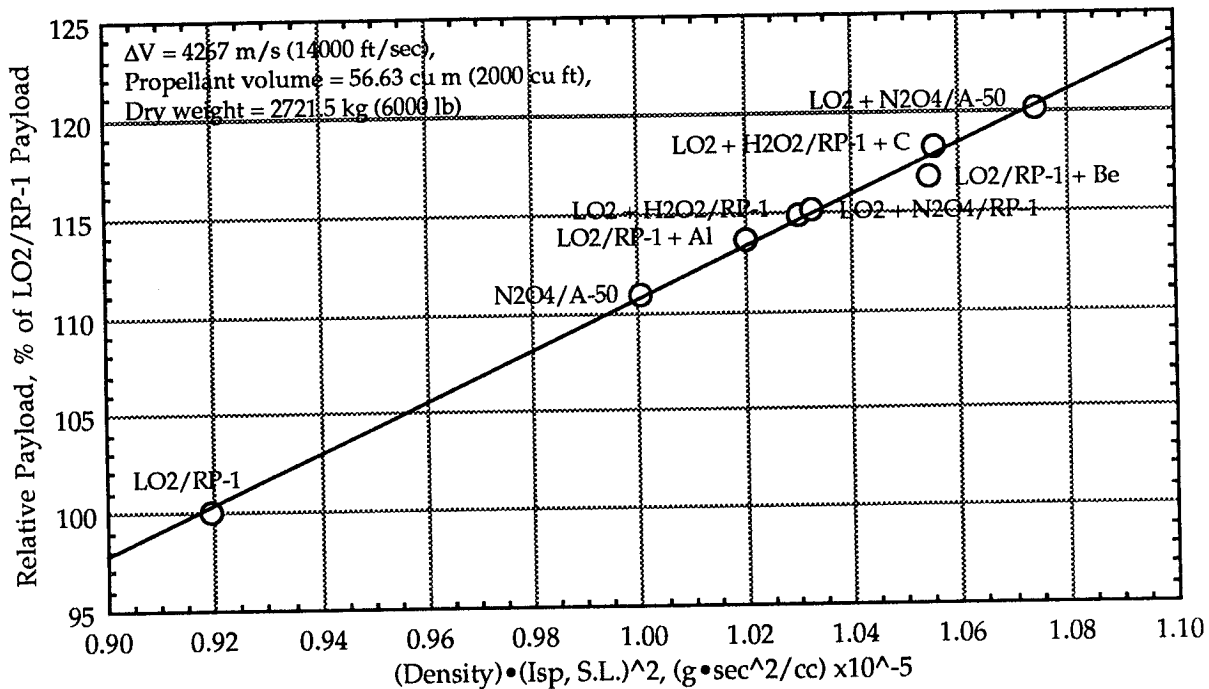


Figure 4. Relative Payloads Using Various Propellants in a Fixed Volume Application

It can be seen from Figure 4 that both $LO_2 + N_2O_4(s)$ and $LO_2 + H_2O_2(s)$ with RP-1 provide higher payloads than $LO_2/RP-1 + Al$, and $LO_2 + N_2O_4(s)$/Aerozine-50 provides a higher payload than $LO_2/RP-1 + Be$. The gelled heterogeneous oxidizer bipropellant combinations should yield somewhat higher combustion efficiencies than the gelled metallized fuel combinations and all the combustion products are gases, thereby eliminating two-phase flow losses and throat erosion. Additionally, RP-1 and Aerozine-50 are more practical thrust chamber coolants and gas generator fuels than the metallized fuels.

The $LO_2 + H_2O_2(s)$/RP-1 + $C(s)$ bipropellant combination is particularly intriguing. It offers a higher payload than $LO_2/RP-1 + Be$, contains only low-environmental-impact elements (carbon,

hydrogen, and oxygen), produces only gaseous combustion products, and should yield a higher percentage of theoretical performance than metallized propellants.

In view of the promising characteristics described above and in response to a NASA Research Announcement (NRA)[3], a proposal was submitted to do research on one member of this new class of dense, cryogenic, gelled, heterogeneous oxidizers. This contract, NAS 3-25822, was awarded to the Aerojet Propulsion Division in December 1989 as a result of that proposal.

### B. PROGRAM OBJECTIVES

The primary objectives of the program were two-fold: (1) to prepare and characterize simple cryogenic oxidizer gels based on liquid oxygen and suitable gelling agents and (2) to prepare and characterize dense, cryogenic, gelled, heterogeneous oxidizers comprised of liquid oxygen as the cryogen, $N_2O_4$ as the dense particulate solid oxidizer, and a suitable gelling agent.

### C. SCOPE OF EFFORT

The program involved six tasks: (1) Task I - Program Definition, (2) Task II - Facility Preparation, (3) Task III - Simple Liquid Oxygen Gel Formulation, (4) Task IV - Heterogeneous Gel Formulation, (5) Task V - Heterogeneous Gel Characterization, and (6) Task VI - Reporting. The accomplishments relevant to Tasks I through V are documented in the following sections. The report is concluded with a summary section and a conclusions and recommendations section.

## II. PROGRAM DEFINITION AND WORK PLAN

### A. PROGRAM DEFINITION

The objective of Task I - Program Definition was to provide detailed test plans to the NASA Project Manager for the gel formulation and characterization efforts. These plans established the framework for performing the facility buildup effort in Task II, formulation work on simple liquid oxygen gels and heterogeneous gels in Tasks III and IV, respectively, and the heterogeneous gel characterization effort in Task V. Task I was completed in December 1989. The result of the effort was a set of work plans for the remaining tasks which were documented in the Basic Contract Work Plan[4]. The original detailed work plans are not repeated here because they changed somewhat in response to accumulating knowledge and experience as the program progressed. The essential elements of the evolved plans are, however, provided in the following section.

## B. WORK PLANS

### 1. Facility Preparation Plan

No hardware, as defined in normal rocket technology test programs, was required to perform the work conducted under this contract. All work was conducted in an existing propellant development laboratory; however, certain special test equipment (laboratory apparatus) was necessary to perform the unique laboratory research required by this program. These special laboratory apparatus were built up from available laboratory items.

Specific elements of work required to accomplish the buildup of the special laboratory apparatus included: (1) the setup of liquid nitrogen-cooled baths for preparing and characterizing the cryogenic gels, (2) buildup of a gel preparation apparatus (gelant injection tube, gel flask, mixer, associated valves, and temperature and pressure sensors), (3) buildup of an $N_2O_4$ particle preparation apparatus ($N_2O_4$ injection tube, particle preparation flask, associated valves, and temperature and pressure sensors), and (4) setup of gel characterization equipment (yield stress, rheological, and gel composition measurement equipment). The special $N_2O_4$ injection tubes used in preparing gels and $N_2O_4$ particles were similar to those used in previous cryogenic gel work.

Upon completion of the setup of the various special apparatus, the gel preparation equipment was checked out on inert materials to assure it functioned properly and in a safe manner. Details of the facility preparation effort are presented in Section III.

### 2. Simple Liquid Oxygen Gel Formulation and Evaluation Plan

Cab-O-Sil (H-5) and $N_2O_4$ were the primary gelants selected to represent the ultra-fine silica and normally-liquid oxidizer types of gelling agents, respectively. Nitric acid, $HNO_3$, was selected as the alternative gelant to be utilized if $N_2O_4$ proved ineffective. Gel formulations using Cab-O-Sil were prepared using a simple high-shear mixing technique similar to that used previously to prepare $N_2O_4$[5], MON-25 (75 % wt $N_2O_4$ and 25 % wt NO)[5], and IRFNA[6] (Inhibited Red Fuming Nitric Acid) gels. Gels formulated with $N_2O_4$ or $HNO_3$ were prepared using a dilute vapor-phase injection method[7] similar to that previously used to gel hydrogen[8,9], methane[10], oxygen difluoride[11], and diborane[11]. Candidate formulations were prepared in nominal 2-liter batches. Where practical and appropriate, simple LOX gels were evaluated on regard to physical stability, density, structure, and viscosity. The gel characterization methods employed are described in the Heterogeneous Gel Characterization Plan, Section II.B.4.

Ultimately, four types of simple cryogenic gels were prepared and evaluated: (1) liquid nitrogen gelled with helium-diluted $N_2O_4$ (for purposes of checking out the laboratory apparatus and

experimental procedures), (2) liquid oxygen gelled with helium-diluted $N_2O_4$, (3) liquid oxygen gelled with oxygen-diluted $N_2O_4$, and (4) liquid oxygen gelled with Cab O- Sil (H-5). The results of these efforts are presented in Section IV.

### 3. Heterogeneous Gel Formulation and Evaluation Plan

The research under this task, Task IV, was comprised of three main elements: (1) the preparation and evaluation of fine particles of solid $N_2O_4$, (2) preliminary formulation and evaluation of heterogeneous liquid oxygen-solid $N_2O_4$ systems, and (3) reformulation and evaluation of heterogeneous gels.

In the first subtask, two basic approaches to preparing fine particles of $N_2O_4$ were pursued and the resulting particles were evaluated in respect to size and shape. The two approaches were: (1) subsurface injection of gaseous $N_2O_4$ mixtures into liquid nitrogen or liquid oxygen and (2) injection of liquid $N_2O_4$ onto the surface of liquid nitrogen or liquid oxygen.

In the second subtask, the $N_2O_4$ particles prepared by the vapor and liquid injection techniques were formulated into two types of heterogeneous slurries containing different loadings and sizes of particles. The two types of slurries were : (1) simple settled slurries and (2) thickened slurries. Evaluations of these two types of slurries defined the approximate upper loading limits for various types/sizes of $N_2O_4$ particles that would be possible in the analogous heterogeneous gel systems.

In the last subtask, heterogeneous gels were formulated using the various types of $N_2O_4$ particles and evaluated in respect to yield stress and density. The detailed results of these efforts are presented in Section V.

### 4. Heterogeneous Gel Characterization Plan

The characterization work under this task, Task V, was comprised of three subtasks: (1) physical stability evaluation, (2) rheological behavior, and (3) physical properties evaluations (i.e., yield stresses and densities). These characterizations were performed on the best simple gels prepared under Task III and the best heterogeneous gels prepared under Task IV.

Physical stability evaluations on the candidate gels involved short-term (< 24 hour) storage under normal gravity at the normal boiling point of liquid nitrogen and subsequent measurement of the volumes of all discernibly different layers.

Rheological characterizations were generally accomplished by viscosity measurements with a Brookfield viscometer operating at various rotational speeds on gels chilled to the normal boiling point of liquid nitrogen. A limited amount of rheological characterization was accomplished by flowing the gel through a coil of tubing and measuring pressure drop and flow rate.

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Physical properties evaluations included the measurement of yield stresses and the calculation of densities. Yield stresses were measured at the normal boiling point of liquid nitrogen by the cone penetrometer method[12]. Densities at the normal boiling point of oxygen were calculated based on measured gel compositions and the known densities of the gel constituents, i.e., liquid oxygen and solid $N_2O_4$. Gel compositions were determined gravimetrically on gel samples by allowing the oxygen to evaporate slowly, leaving the solid $N_2O_4$ behind.

## III. TEST APPARATUS AND EXPERIMENTAL METHODS

All work on this program was conducted within existing test facilities consisting primarily of a propellant development laboratory and its associated test bays. No hardware, as defined in normal rocket technology test programs, was required to perform the work. However, laboratory-type apparatus unique to this very specialized type of gelation work were required. The preparation of these unique facilities is summarized in the following sections.

### A. GENERAL FACILITY

The gel preparation and characterization research was conducted in a general purpose test bay (Chemistry Bay 5, Bldg. 30-002) which is closed on three sides and covered by a roof for weather protection. It provided electric power, lighting, ventilation, water, gaseous and liquid nitrogen services, and close access to a control room and data acquisition equipment. Supplies of gaseous oxygen and helium were provided from compressed gas cylinders located in the test bay. Liquid oxygen was supplied from a 0.16 $m^3$ (42 gal) Dewar.

### B. INTEGRATED GEL PREPARATION AND CHARACTERIZATION APPARATUS

An integrated gel preparation and characterization apparatus was designed and assembled for this program. It incorporated refinements on systems which evolved from several earlier cryogenic gel efforts on hydrogen[8,9], methane[10], oxygen diflouride[11], and diborane[11]. The overall system, as assembled for this program, is shown diagrammatically in Figure 5. It featured a gel preparation vessel (GPV1), two sets of flow coils (FC1 and FC2), and two catch vessels (CV1 and CV2), all of which were immersed in a liquid nitrogen bath contained in a single large stainless steel Dewar approximately 0.9 m (3 ft) in dia. and 0.6 m (2 ft) deep. The system also included a means of adding liquid nitrogen to make up for evaporation, a periscope for the subsurface viewing of any of the vessels in the liquid nitrogen bath, and a saturator (SV1) for preparing dilute gaseous $N_2O_4$ as a gelant feed stream to GPV1 via the special gaseous gelant injection tube. A schematic diagram of the special
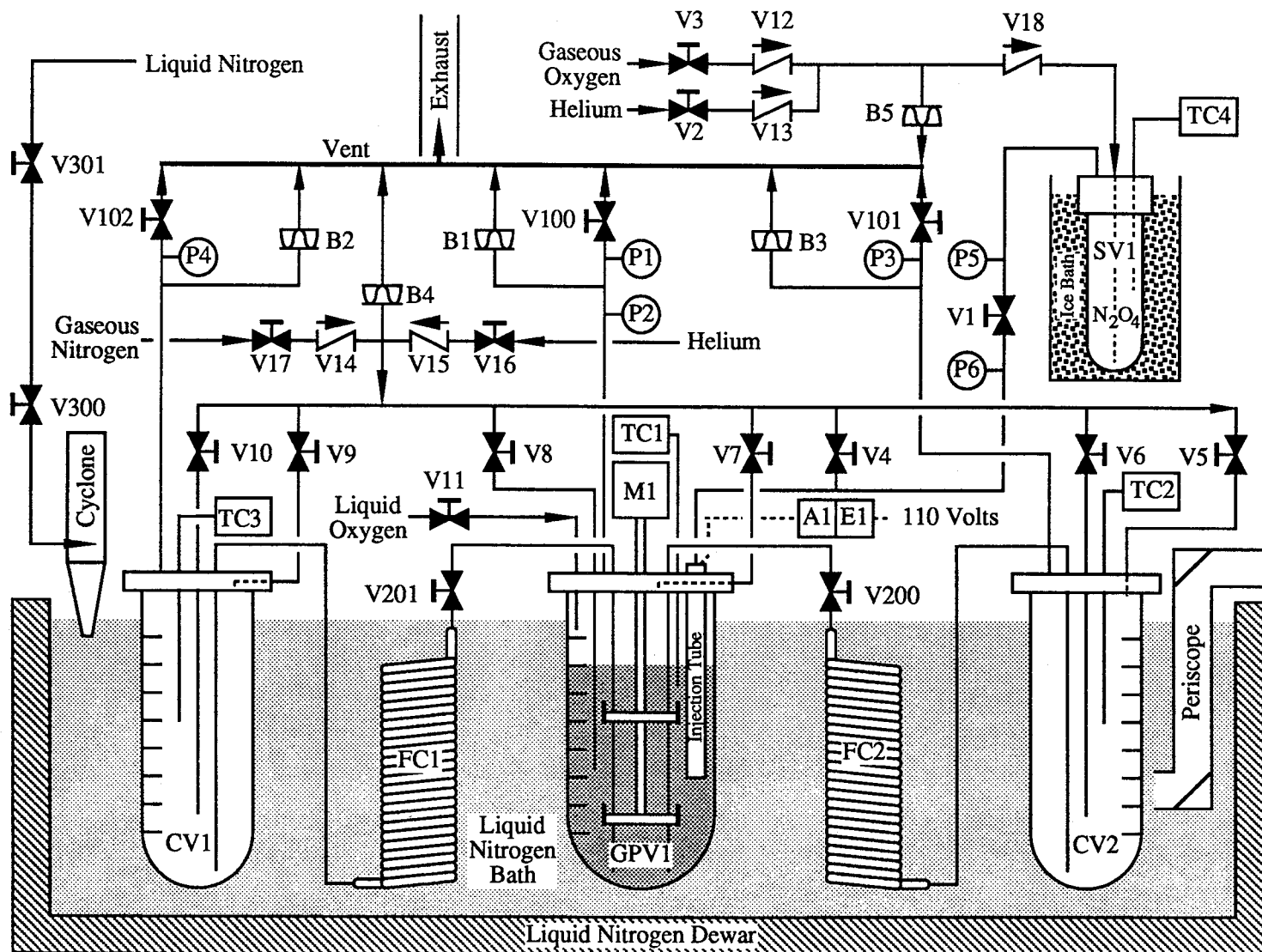
Figure 5. Schematic Diagram of the Integrated Gelled Cryogenic Oxidizer Preparation and Characterization Apparatus

vacuum-jacketed, internally-heated, gelant injection tube is shown in Figure 6. The components comprising this overall system are described and their functions identified in Table II.

The integrated system was used primarily for performing heterogeneous gel characterization work under Task V where flow tests and physical stability evaluations were of major interest. For the gel formulation and evaluation research conducted under Tasks III and IV, the integrated apparatus was found to be experimentally cumbersome and provided poor visibility into the gel preparation vessel. Thus, most of the gel formulation and evaluation work was conducted in simplified apparatuses which featured only the pertinent subsystems contained in smaller clear glass Dewars. These simplified apparatus are discussed in the following section.

## C. SIMPLIFIED GEL PREPARATION AND EVALUATION APPARATUS

### 1. Liquid Oxygen Gel Preparation Apparatuses and Procedures

Two different apparatuses were used to prepare simple liquid oxygen gels under Task III depending on the gelling agent employed. Both utilized the gel preparation subsystem from the integrated apparatus shown in Figure 5, i.e., the gel preparation vessel (GPVI) and certain of its associated components.

For the preparation of gels formed with gaseous $N_2O_4$ mixtures, the apparatus was configured as shown diagrammatically in Figure 7. Gels were prepared by adding liquid oxygen to GPV1 via valve V11 and adding gaseous gelant mixture from the $N_2O_4$ saturator SV1 via valve V1 and the gelant injection tube (see Figure 6). Agitation was provided by the bubbling action of the injection tube (or by bubbling helium into the liquid oxygen via valve V8). The composition of the gelant gas mixture was controlled by selection of the desired diluent gas (oxygen or helium) via valve V3 or V2 and appropriate control of the operating temperature (TC4) and pressure (P5) in the $N_2O_4$ saturator.

Gels formed using Cab-O-Sil (H-5) as the gelling agent were prepared in the apparatus shown diagrammatically in Figure 8. Gels were prepared by adding predried and prechilled Cab-O-Sil (H-5) to GPV1 via a tee in its vent line, adding liquid oxygen via its fill valve V11, and stirring with a dual turbine, high-shear mixer which was driven by a variable speed motor M1.

### 2. Nitrogen Tetroxide Particle Preparation Apparatus and Procedures

Solid particles of $N_2O_4$ were prepared in apparatuses configured essentially the same as those shown in Figures 7 or 8, depending on the size of particles desired.

Very small particles were prepared in the apparatus shown in Figure 7. The procedure involved first filling GPV1 with the appropriate cryogen , i.e. liquid nitrogen or liquid oxygen, and

Electrical Leads

Insulated
Lead-through

N₂O₄ or Gelant/
Gas Mixture

Outer
Jacket

Heater
Assembly

Inner
Jacket

Vacuum
Jacket

4-Hole
Alumina
Insulator

5-mil Resistance
Heating Wire
(section view)
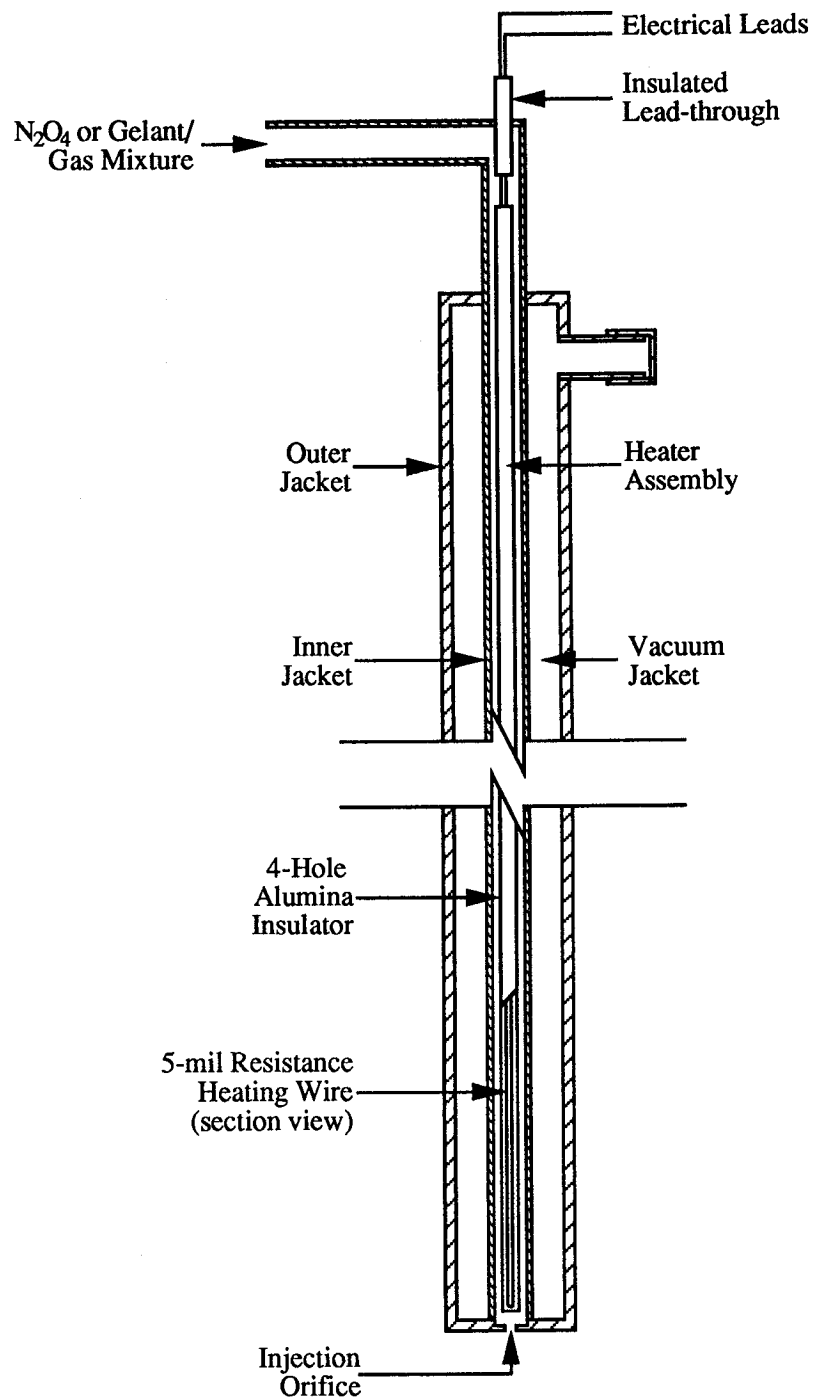
Injection
Orifice

Figure 6. Schematic Diagram of Vacuum-Jacketed, Internally-Heated, Injection Tube

# Table II

## Test Equipment and Instrumentation List

| Item | Description/Function |
|------|---------------------|
| A1 | Ammeter, electric current to injection tube heater |
| A2 | Ammeter, electric current to the heater on the nitric acid saturator |
| B1 | Burst disk safety for GPV1, 791 kPa (100 psig) |
| B2 | Burst disk safety for CV1, 791 kPa (100 psig) |
| B3 | Burst disk safety for CV2, 791 kPa (100 psig) |
| B4 | Burst disk safety in helium/nitrogen supply, 791 kPa (100 psig) |
| B5 | Burst disk safety in gas supply to saturator SV1, 2170 kPa (300 psig) |
| CV1 | Catch vessel #1 for viscosity measurements, approximately 1 liter |
| CV2 | Catch vessel #2 for viscosity measurements, approximately 1 liter |
| Cyclone | Gas/liquid separator for liquid nitrogen supply |
| E1 | Variac, electric power controller for injection tube heater |
| E2 | Variac, electric power controller to the heater on the nitric acid saturator |
| FC1 | Flow coil #1, 3.175 mm OD (1/8") or 4.7625 mm OD (3/16") |
| FC2 | Flow coil #2, 6.35 mm OD (1/4") or 7.9375 mm OD (5/16") |
| GPV1 | Gel preparation vessel, approximately 3 liters |
| Ice Bath | Ice bath for $N_2O_4$ saturator |
| Injec. Tube | Gaseous gelant injection tube for GPV1 |
| $LN_2$ Dewar | Liquid nitrogen bath for CV1, CV2, FC1,FC2, and GPV1 |
| M1 | Stirrer motor for GPV1 |
| P1 | GPV1 pressure gauge, 0-791 kPa (0-100 psig) |
| P2 | GPV1 pressure transducer, 0-791 kPa (0-100 psig) |
| P3 | CV2 pressure transducer, 0-791 kPa (0-100 psig) |
| P4 | CV1 pressure transducer, 0-791 kPa (0-100 psig) |
| P5 | Saturator SV1 pressure gauge, 0-1480 kPa (0-200 psig) |
| P6 | Gelant pressure gauge, 0-1480 kPa (0-200 psig) |
| Periscope | Periscope for subsurface viewing in liquid nitrogen bath |
| SV1 | Saturator vessel for preparing gaseous $N_2O_4$ or $HNO_3$ gelants |
| TC1 | Temperature in GPV1 |
| TC2 | Temperature in CV2 |
| TC3 | Temperature in CV1 |
| TC4 | Temperature in saturator SV1 |
| V1 | Gaseous gelant supply valve from saturator SV1 to injection tube |
| V2 | Helium/nitrogen supply valve to saturator SV1 |
| V3 | Gaseous oxygen supply valve to saturator SV1 |
| V4 | Helium/nitrogen purge valve to injection tube |
| V5 | Helium/nitrogen pressurant valve to CV2 |
| V6 | Helium/nitrogen sparge valve to CV2 |
| V7 | Helium/nitrogen pressurant valve to GPV1 |
| V8 | Helium/nitrogen sparge valve to GPV1 |
| V9 | Helium/nitrogen pressurant valve to CV1 |
| V10 | Helium/nitrogen sparge valve to CV1 |
| V11 | Liquid oxygen fill valve |
| V12 | Gaseous oxygen supply system check valve |
| V13 | Check valve in helium/nitrogen supply system to saturator SV1 |
| V14 | Gaseous nitrogen supply system check valve |
| V15 | Gaseous helium supply system check valve |
| V16 | Main helium supply shutoff valve |
| V17 | Main gaseous nitrogen supply shutoff valve |
| V18 | Check valve in gas supply to saturator SV1 |
| V100 | GPV1 vent valve |
| V101 | CV2 vent valve |
| V102 | CV1 vent valve |
| V200 | GPV1 shutoff valve to FC2 and CV2 |
| V201 | GPV1 shutoff valve to FC1 and CV1 |
| V300 | Liquid nitrogen supply shutoff valve |
| V301 | Liquid nitrogen supply control valve |
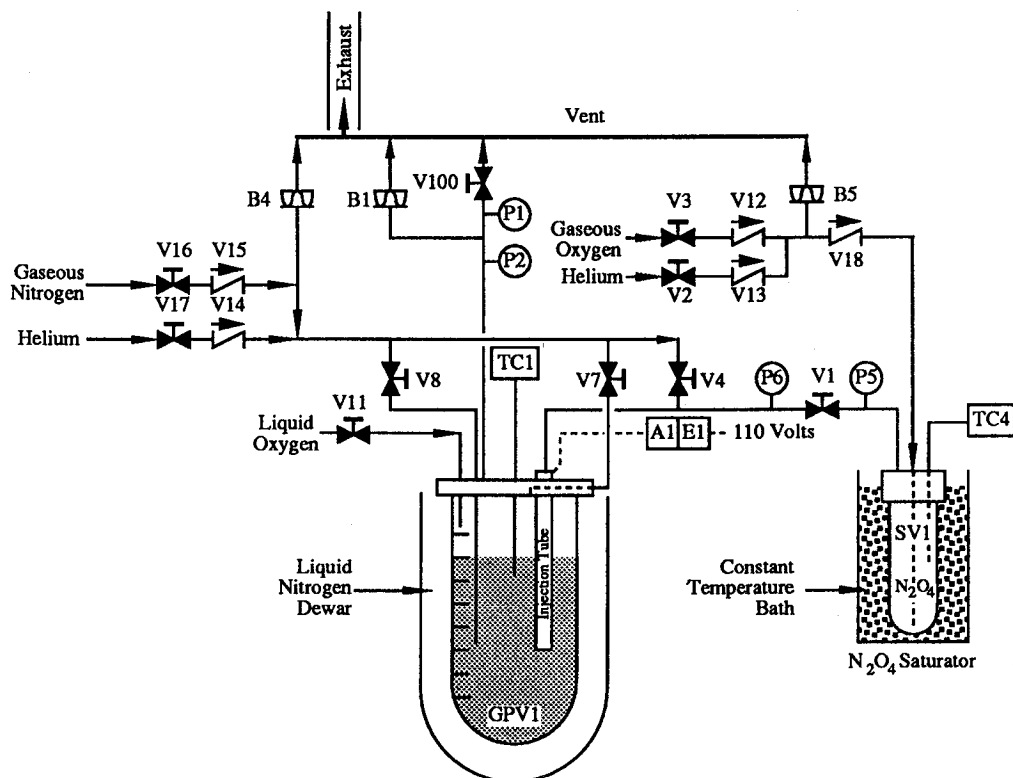
**Figure 7. Schematic Diagram of Apparatus Used To Prepare Gels Formed with Nitrogen Tetroxide/Carrier Gas**
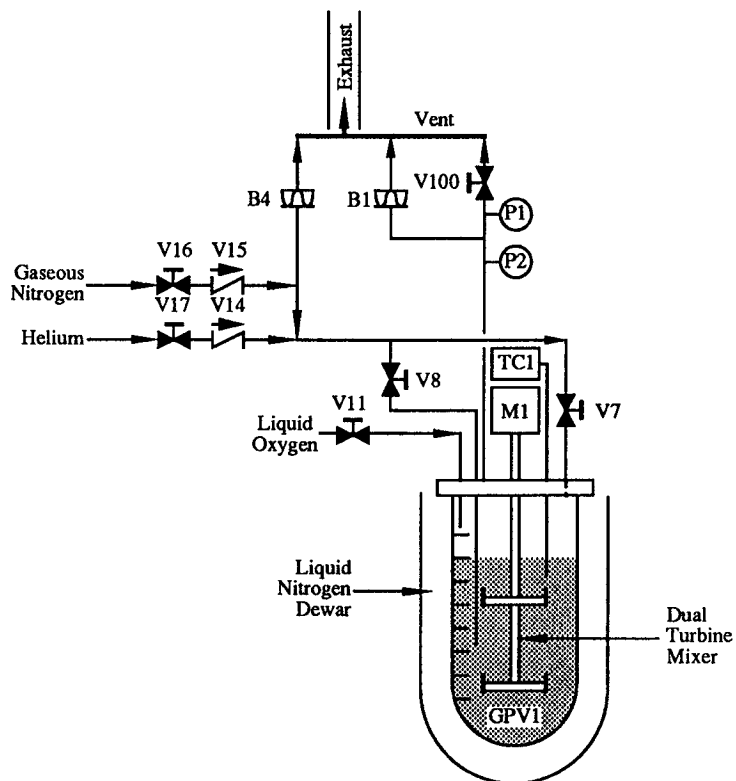


**Figure 8. Schematic Diagram of Apparatus Used To Prepare Gels Formed with Cab-O-Sil (H-5)**

then injecting an appropriate gaseous $N_2O_4$ mixture into the cryogen using the gelant injection tube. Generally, the gas mixtures employed here were richer in $N_2O_4$ than those used for preparing simple gels.

Somewhat larger particles of $N_2O_4$ were prepared in an apparatus very similar to that shown in Figure 8 except for the addition of a helium-pressurized supply of liquid $N_2O_4$ which fed a miniature, single-orifice, hydraulic nozzle. The nozzle was positioned normal to liquid surface and directed a spray of small liquid droplets of $N_2O_4$ onto the surface of a cryogenic liquid. The procedure involved filling the GPV1 with liquid nitrogen or liquid oxygen and then injecting $N_2O_4$ droplets onto the surface of the oxygen. Generally, the surface was agitated by the action of the mixer.

## 3. Heterogeneous Gel Preparation Apparatus and Procedures

The preparation of heterogeneous gels generally involved a three-step process and the use of the simplified apparatuses discussed in the two preceding sections. The first step was the preparation of a suspension of $N_2O_4$ particles in liquid oxygen. It was accomplished in one of the $N_2O_4$ particle preparation apparatuses described above. The apparatus selected and its operating conditions depended upon the nature of particles (size and shape) desired. The suspension of solid $N_2O_4$ particles in liquid oxygen were then subjected to the gelation process utilizing the apparatus shown in Figure 7. After an appropriate gelant addition period, the heterogeneous solid $N_2O_4$-liquid oxygen system was sparged with helium to remove excess oxygen and provide agitation to maintain a uniform dispersion. The sparging was continued until the mixture developed sufficient structure to prevent settling in the absence of agitation.

## 4. Gel Characterization Apparatus and Methods

The gels were evaluated in respect to five characteristics: (1) composition, (2) particle nature, (3) physical stability, (4) rheological behavior, and (5) physical properties. Because of the limited scope of the program, some of the characterizations were necessarily of a preliminary or cursory nature.

### a. Compositions

Compositions of the gels (or thick slurries) were determined gravimetrically by placing weighed samples into a small, tared Dewar which was prechilled with liquid nitrogen. The oxygen (or nitrogen) in the sample was allowed to evaporate slowly until a constant residual weight was achieved at a temperature slightly above the boiling point of liquid oxygen. The residual weight of solid $N_2O_4$ (or Cab-O-Sil) defined the weight fractions of liquid oxygen and $N_2O_4$ or Cab-O-Sil,

respectively. From the weight fractions and known densities of liquid oxygen and solid $N_2O_4$ (see Appendix A) and of Cab-O-Sil ($\approx$ 2200 kg/m$^3$, 137 lb/ft$^3$), volumetric compositions were calculated assuming additive volumes, i.e., negligible solubility of $N_2O_4$ and/or Cab-O-Sil in liquid oxygen.

## b. Particle Nature

The nature of the $N_2O_4$ particles (size and shape) in cryogenic slurries or gels was characterized by two methods: (1) from sedimentation rates in liquid oxygen and (2) by observation of dispersions in liquid nitrogen using a binocular microscope with a calibrated eyepiece. Because of the small particle sizes, agglomeration was a common occurrence which caused difficulty in discriminating between the characteristics of individual particles and those of agglomerates.

In the sedimentation evaluations, a small amount of slurry or gel was placed in a graduated cylinder of liquid oxygen immersed in a Dewar containing liquid nitrogen. Terminal settling velocities were defined by measuring the time required for the bulk of the $N_2O_4$ particles to settle a given distance. Equivalent spherical particles sizes were then calculated from classical relationships between particle size and terminal settling velocity. These relationships are given in Appendix B.

Observation with a microscope was performed by dropping a small amount of slurry or gel into boiling liquid nitrogen contained in a prechilled watchglass. As the nitrogen boiled away, a residue of solid $N_2O_4$ particles remained on the watchglass and could be observed for about 15 to 30 s before the particles began to melt. During that period, the observations for determining approximate particle size and shape were performed.

## c. Physical Stability

The physical stabilities of slurries and heterogeneous gels were determine by observing the mixtures in volume-calibrated glass vessels at constant temperature in a liquid nitrogen bath or Dewar. The formation of distinct layers was taken as an indication of physical instability and the volume fraction of supernatant liquid was used to quantify the extent of the instability. In the majority of the evaluations, the observations were performed over a 1-hour period. The storage period was extended to approximately 12 hours in one case.

## d. Rheological Behavior

The rheological characteristics of gels were generally determined at the normal boiling point of nitrogen using a rotational viscometer (Brookfield, Model LVF with spindle #4) operating at rotational speeds of 6, 12, 30, and 60 rev/min. The increasing rotational speeds represent increasing

shear rates. Gel samples were placed in an insulated container which was prechilled with liquid nitrogen as was the spindle of the viscometer. Viscosity measurements at the various rotational speeds defined relationships between viscosities and shear rates.

In one case, the viscosity of a gel was determined in the integrated apparatus shown in Figure 5. It was accomplished by flowing the gel from GPV1 through a 15.2-m (50-ft) coil of tubing (FC1) into a catch vessel (CV1) and measuring both pressure drop across the coil (P2-P4) and volumetric flow rate. From those measurements and the flow coil geometry, the shear stress, shear rate, and viscosity of the gel were calculated from classical rheological relationships (see Appendix C).

### e. Physical Properties

Physical property characterizations were limited to determinations of densities and yield stresses. Gel densities were derived from compositional data and from knowledge of the densities of the gel components (see section III.C.4.a. and Appendix A) assuming the component volumes were additive, i.e., $N_2O_4$ and Cab-O-Sil have negligible solubility in liquid oxygen. Experience in several earlier heterogeneous gel programs has shown such an assumption to be very nearly correct and the derived densities to agree with directly measured density values within experimental error.

Yield stresses were measured with a cone penetrometer using a modification of the method given in ASTM-D-217. The apparatus and method are described in detail in Liquid Propellant Test Methods[12]. To apply the storable gel test method to cryogenic gels, samples of the gels were placed in an insulated container which was prechilled with liquid nitrogen as were the cone and shaft of the cone penetrometer. Otherwise, the methodology was similar to that published for storable gels.

## D. DATA ACQUISITION

Experimental data were acquired both manually and via a digital minicomputer/data logger/display system. Information relative to formulation procedures, parameters, observations, and gel characteristics were normally acquired manually and recorded in a research laboratory notebook. A few key operating parameters (i.e., temperatures and pressures) were continuously displayed digitally to aid in the monitoring of gel preparations. In the case of gel flow tests, pressure drops across the test section and flow information were digitally recorded with the minicomputer system for subsequent data reduction and analysis.

## E. CRITICAL EXPERIMENT REVIEW

Prior to starting experimental work, a critical experiment review (CER) was held to assure that the test system and test plan were consistent with program objectives, safety and environmental

considerations, and minimized risks to personnel and property. That formal multidisciplinary peer review provided a forum for the critical assessment of the planned work before and actual experiments were conducted

## F. FACILITY CHECKOUT

Subsequent to the critical experiment review, two facility checkout tests were performed. The tests involved the checkout of the $N_2O_4$ gelant preparation subsystem, SV1, using helium diluent and injection of the dilute $N_2O_4$ gaseous gelant into liquid nitrogen via the vacuum-jacketed, internally-heated, injection tube. Those tests established three significant facts: (1) the gaseous $N_2O_4$ gelant preparation subsystem functioned properly over a range of helium dilutions, (2) the gelant injection tube functioned well over a range of helium dilutions without freeze-up, and (3) extremely small $N_2O_4$ particles were formed in sufficient quantity to produce liquid nitrogen gels. The first two facts provided confidence that the facility was functional and ready for experimental work. The last fact was the first proof-of-principle demonstration that minute $N_2O_4$ particles would gel liquid nitrogen, giving confidence that liquid oxygen could be similarly gelled.

## IV. FORMULATION AND EVALUATION OF SIMPLE CRYOGENIC GELS

Four types of simple cryogenic gels were prepared and evaluated under Task III:
1. Liquid nitrogen gelled with helium-diluted $N_2O_4$
2. Liquid oxygen gelled with helium-diluted $N_2O_4$
3. Liquid oxygen gelled with oxygen-diluted $N_2O_4$
4. Liquid oxygen gelled with Cab-O-Sil (H-5)

The research conducted on each of these four types of gels is summarized in the following sections.

### A. SIMPLE LIQUID NITROGEN GELS PREPARED WITH NITROGEN TETROXIDE/ HELIUM GELANT

Two series of liquid nitrogen gels were prepared using helium-diluted $N_2O_4$ (3.6 and 7.9 % vol $N_2O_4$, respectively) as the gelling agent. A dilute vapor-phase injection method was used in each case to introduce the gaseous gelant ($N_2O_4$) into the liquid nitrogen. These tests served to checkout the test equipment and provided the first proof-of-principle demonstration of the efficacy of $N_2O_4$ as a gelant for a nonpolar cryogen.

The characteristics of these preliminary liquid nitrogen/$N_2O_4$ gels are summarized in Table III. Gels containing about 2.0 to 19.6 % vol (4.9 to 37.4 % wt) $N_2O_4$ were studied. None of these gels

Table III

Characteristics of Simple Liquid Nitrogen/Nitrogen Tetroxide Gels [1]

| Gel Identification: C-1 | | | | | Gelant: 3.64 % vol N2O4 in He | |
|---|---|---|---|---|---|---|
| Cryogen: Liquid Nitrogen at 77.35 K (NBP of Nitrogen) | | | | | | |
| Gelant Concentration in the Gel Layer | | Super-natant, | Gel Density [2] | | Yield Stress [3] | |
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm |
| 4.88 | 2.05 | 0 | 832 | 0.832 | ≈ 10 | ≈ 100 |
| 8.35 | 3.59 | 0 | 850 | 0.850 | ≈ 20 | ≈ 200 |
| 11.0 | 4.78 | 0 | 864 | 0.864 | ≈ 30 | ≈ 300 |
| 15.9 | 7.18 | 0 | 892 | 0.892 | 60-70 | 600-700 |
| 17.5 | 7.97 | 0 | 901 | 0.901 | 90-100 | 900-1000 |

| Gel Identification: C-2 | | | | | Gelant: 7.86 % vol N2O4 in He | |
|---|---|---|---|---|---|---|
| Cryogen: Liquid Nitrogen at 77.35 K (NBP of Nitrogen) | | | | | | |
| Gelant Concentration in the Gel Layer | | Super-natant, | Gel Density [2] | | Yield Stress [3] | |
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm |
| 5.80 | 2.45 | 0 | 837 | 0.837 | ≈ 10 | ≈ 100 |
| 9.09 | 3.92 | 0 | 854 | 0.854 | ≈ 20 | ≈ 200 |
| 14.6 | 6.54 | 0 | 885 | 0.885 | ≈ 50 | ≈ 500 |
| 21.0 | 9.80 | 0 | 923 | 0.923 | ≈ 100 | ≈ 1000 |
| 26.9 | 13.1 | 0 | 961 | 0.961 | ≈ 140 | ≈ 1400 |
| 37.4 | 19.6 | 0 | 1038 | 1.038 | Paste | Paste |

[1] All gel characteristics defined at the normal boiling point (NBP) of liquid nitrogen.
[2] Calculated values based on component densities (liquid nitrogen = 808.1 kg/cu m, solid nitrogen tetroxide = 1979 kg/cu m).
[3] Approximate values based on estimates by an experienced researcher.
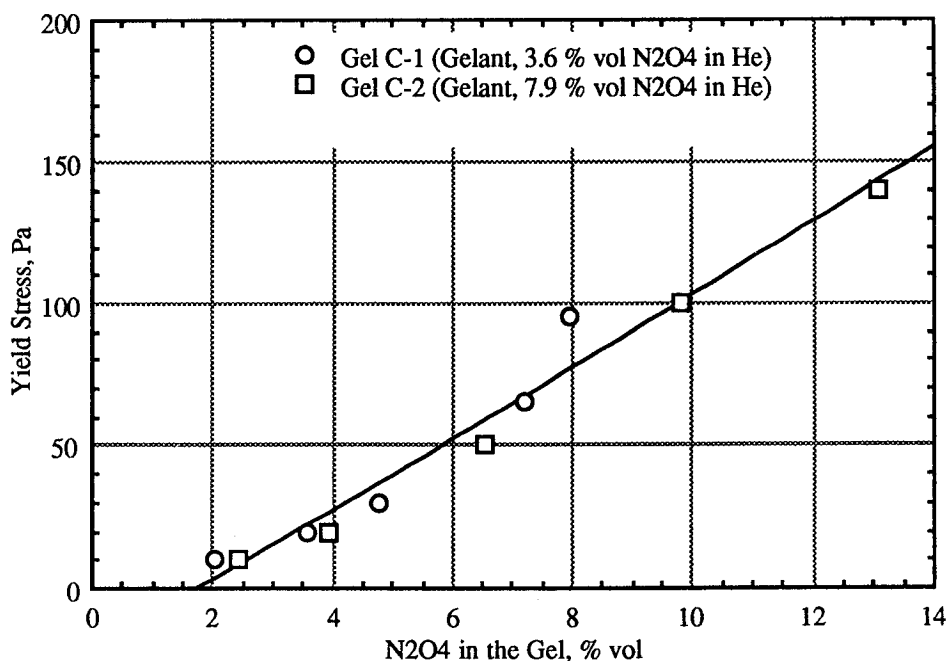


Figure 9. Estimated Yield Stress of Liquid Nitrogen/Nitrogen Tetroxide Gels

exhibited evidence of settling in short-term ($\approx$ 30 min.) observations of physical stability. The approximate yield stresses of the gels are shown in Figure 9 as a function of $N_2O_4$ gelant concentration. Figure 9 clearly shows that both series of gels had similar strengths at similar gelant concentrations. This indicates that both $N_2O_4$ concentrations in the injected $N_2O_4$-He gas mixture (i.e., 3.6 and 7.9 % vol) were approximately equally effective in gelling liquid nitrogen. Extrapolation of the curves in Figure 9 to zero yield stress indicates that the minimum concentration of $N_2O_4$ required to achieve the onset of gelation is about 1.8 % vol (4.0 % wt). The concentration required to produce a moderately strong gel (i.e., one having a yield stress of 100 Pa, 1000 dynes/$cm^2$) is approximately 9.5 % vol (21 % wt).

## B. SIMPLE LIQUID OXYGEN GELS PREPARED WITH NITROGEN TETROXIDE/HELIUM GELANT

Three series of liquid oxygen gels were prepared using helium-diluted $N_2O_4$ (4.4, 16.6, and 48.4 % vol $N_2O_4$, respectively) as the gelling agent. A dilute vapor-phase injection method was used in each case to introduce the gaseous gelant into the liquid oxygen. These series of gels were prepared to define the effect of the concentration of $N_2O_4$ in the injected $N_2O_4$ -He gas mixture on its effectiveness as a gelling agent.

The characteristics of these liquid oxygen/$N_2O_4$ gels are summarized in Table IV. Gels containing 2.7 to 23 % vol (4.4 to 33% wt) $N_2O_4$ were studied. As can be seen in Table IV, only gel series C-9 and C-7 exhibited tendencies to settle (i.e., form a supernatant layer upon standing). This behavior occurred only at the lowest concentrations of $N_2O_4$. Yield stresses of the gels are shown in Figure 10 as functions of $N_2O_4$ concentration. Figure 10 clearly indicates that the dilute $N_2O_4$-He mixture (4.4 % vol $N_2O_4$) used to prepare the C-3 series of gels is a more effective gelant than those used to prepare the C-9 and C-7 series of gels which contained 16.6 and 48.4 % vol $N_2O_4$ in He. With the dilute gelant, the onset of gelation was achieved at about 1.8 % vol $N_2O_4$ whereas approximately 7 % vol was required when the more concentrated gelants were used. The concentrations of $N_2O_4$ in the gels necessary to produce yield stresses of 100 Pa (1000 dynes/$cm^2$) were approximately 8.5, 10.0, and 11.5 % vol, using the three different $N_2O_4$-He gas mixtures as gelants. Interestingly, the dilute gelant used in formulating the C-3 liquid oxygen gels exhibited essentially the same effectiveness as the dilute gelants used to formulate the C-1 and C-2 liquid nitrogen gels (see Figure 9).

Viscosity data were successfully measured on the C-9 series of gels using a Brookfield viscometer at 6 revolutions per minute (RPM). The viscosities versus $N_2O_4$ concentration in the gel are shown in Figure 11. Extrapolation of the curve to a viscosity near that of ungelled liquid oxygen (i.e., $2.9 \times 10^{-4}$ Pa•s) indicates that the onset of gelation occurs at an $N_2O_4$ concentration of approximately 7% vol, a value consistent with that obtained by extrapolating the yield stress-concentration curve (Figure 10).

**Table IV**

**Characteristics of Simple Liquid Oxygen Gels Prepared with N2O4/He Gelant**

| Gel Identification: C-3 | | | | | | Gelant: 4.43 % vol N2O4 in He | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cryogen: Liquid Oxygen at 90.18 K (NBP of Oyxgen) | | | | | | | | | | |
| Gelant Conc. in Gel Layer | | Super-natant, | Gel Density [1] | | Yield Stress [2] | | Visc., Pa·s [3] | | Visc., cp [3] | |
| | | | | | | | 6 RPM | 12 RPM | 6 RPM | 12 RPM |
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm | | | | |
| 4.38 | 2.71 | 0 | 1227 | 1.227 | ≈ 10 | ≈ 100 | — | — | — | — |
| 7.56 | 4.54 | 0 | 1184 | 1.184 | ≈ 30 | ≈ 300 | — | — | — | — |
| 11.14 | 6.81 | 0 | 1206 | 1.206 | ≈ 60 | ≈ 600 | — | — | — | — |
| 13.74 | 8.51 | 0 | 1222 | 1.222 | ≈ 100 | ≈ 1000 | — | — | — | — |
| 17.92 | 11.35 | 0 | 1249 | 1.249 | >100 | >1000 | — | — | — | — |
| 25.78 | 17.03 | 0 | 1303 | 1.303 | Thick | Thick | — | — | — | — |
| 33.00 | 22.70 | 0 | 1356 | 1.356 | V. Thick | V. Thick | — | — | — | — |

Note: Gel C-3 initially prepared at NBP of N2 and subsequently allowed to warm to NBP of O2. Gel characteristics defined at the NBP of O2 except for first data entry (at NBP of N2).

| Gel Identification: C-9 | | | | | | Gelant: 16.6 ± 0.6 % vol N2O4 in He | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cryogen: Liquid Oxygen at 77.35 K (NBP of Nitrogen) | | | | | | | | | | |
| Gelant Conc. in Gel Layer | | Super-natant, | Gel Density [1] | | Yield Stress [4] | | Visc., Pa·s [3] | | Visc., cp [3] | |
| | | | | | | | 6 RPM | 12 RPM | 6 RPM | 12 RPM |
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm | | | | |
| 10.83 | 6.88 | 5.26 | 1256 | 1.256 | — | — | — | — | — | — |
| 12.12 | 7.73 | 0.00 | 1263 | 1.263 | — | — | — | — | — | — |
| 12.36 | 7.89 | 0.00 | 1264 | 1.264 | 18.5 | 185 | 0.167 | — | 167 | — |
| 14.08 | 9.06 | 0.00 | 1273 | 1.273 | 37.4 | 374 | 0.383 | 0.25 | 383 | 250 |
| 15.81 | 10.24 | 0.00 | 1282 | 1.282 | 132.7 | 1327 | 0.583 | >0.83 | 583 | >830 |
| 16.45 | 10.69 | 0.00 | 1286 | 1.286 | 190.8 | 1908 | >1.67 | — | >1670 | — |
| 19.69 | 12.97 | 0.00 | 1303 | 1.303 | 254.4 | 2544 | — | — | — | — |

Note: Gel C-9 characteristics defined at the normal boiling point (NBP) of liquid nitrogen

| Gel Identification: C-7 | | | | | | Gelant: 48.4 ± 1.3% vol N2O4 in He | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Cryogen: Liquid Oxygen at 77.35 K (NBP of Nitrogen) | | | | | | | | | | |
| Gelant Conc. in Gel Layer | | Super-natant, | Gel Density [1] | | Yield Stress [4] | | Visc., Pa·s [3] | | Visc., cp [3] | |
| | | | | | | | 6 RPM | 12 RPM | 6 RPM | 12 RPM |
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm | | | | |
| 11.20 | 7.12 | 2.56 | 1258 | 1.258 | — | — | — | — | — | — |
| 11.22 | 7.13 | 0.00 | 1258 | 1.258 | 5.9 | 59 | — | — | — | — |
| 12.32 | 7.87 | 0.00 | 1264 | 1.264 | 20.2 | 202 | — | — | — | — |
| 14.04 | 9.03 | 0.00 | 1273 | 1.273 | 32.7 | 327 | — | — | — | — |
| 14.30 | 9.21 | 0.00 | 1274 | 1.274 | 30.8 | 308 | — | — | — | — |
| 15.91 | 10.31 | 0.00 | 1283 | 1.283 | — | — | — | — | — | — |
| 17.15 | 11.17 | 0.00 | 1290 | 1.290 | 69.6 | 696 | >1.67 | — | >1667 | — |
| 18.89 | 12.40 | 0.00 | 1299 | 1.299 | 259 | 2594 | — | — | — | — |

Note: Gel C-7 characteristics defined at the normal boiling point (NBP) of liquid nitrogen

[1] Calculated values based on component densities (LO2, 1141 and 1202.8 kg/cu m at 90.18 and 77.35 K, respectively; solid N2O4, 1972 and 1979 kg/cu m at 90.18 and 77.35 K, respectively).
[2] Visually estimated values
[3] Determined with a Brookfield viscometer.
[4] Determined with a cone penetrometer.
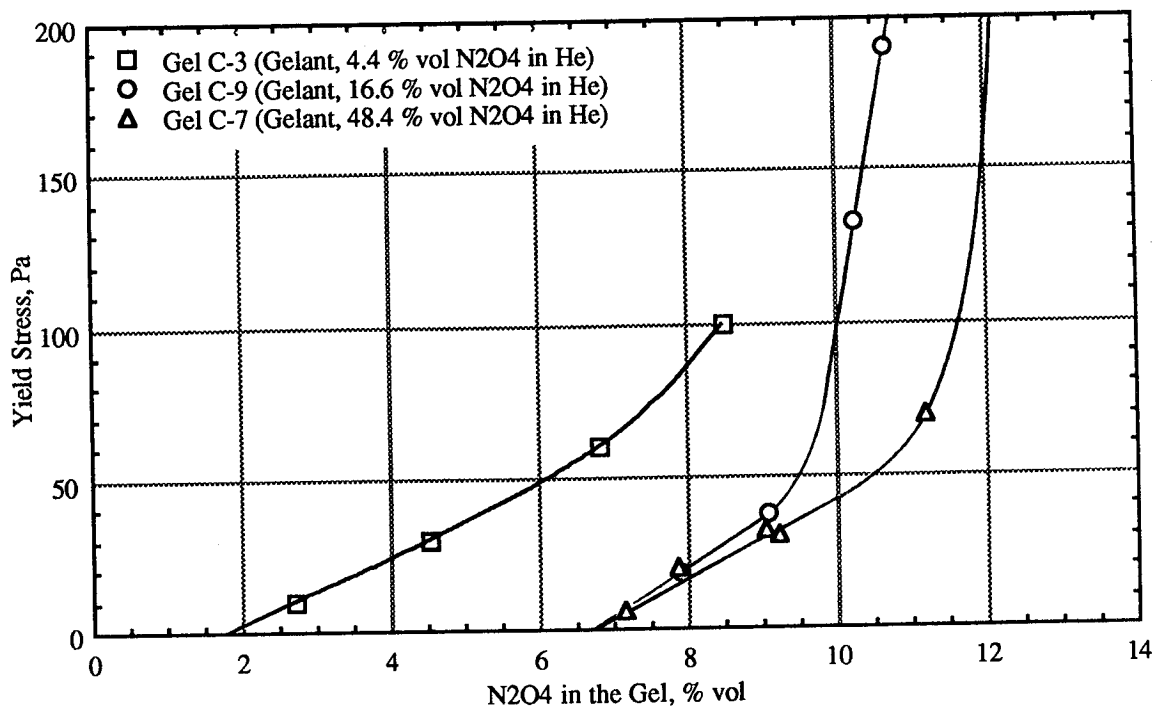
Figure 10. Yield Stress of Liquid Oxygen/Nitrogen Tetroxide Gels Prepared with
Nitrogen Tetroxide-Helium Gelants
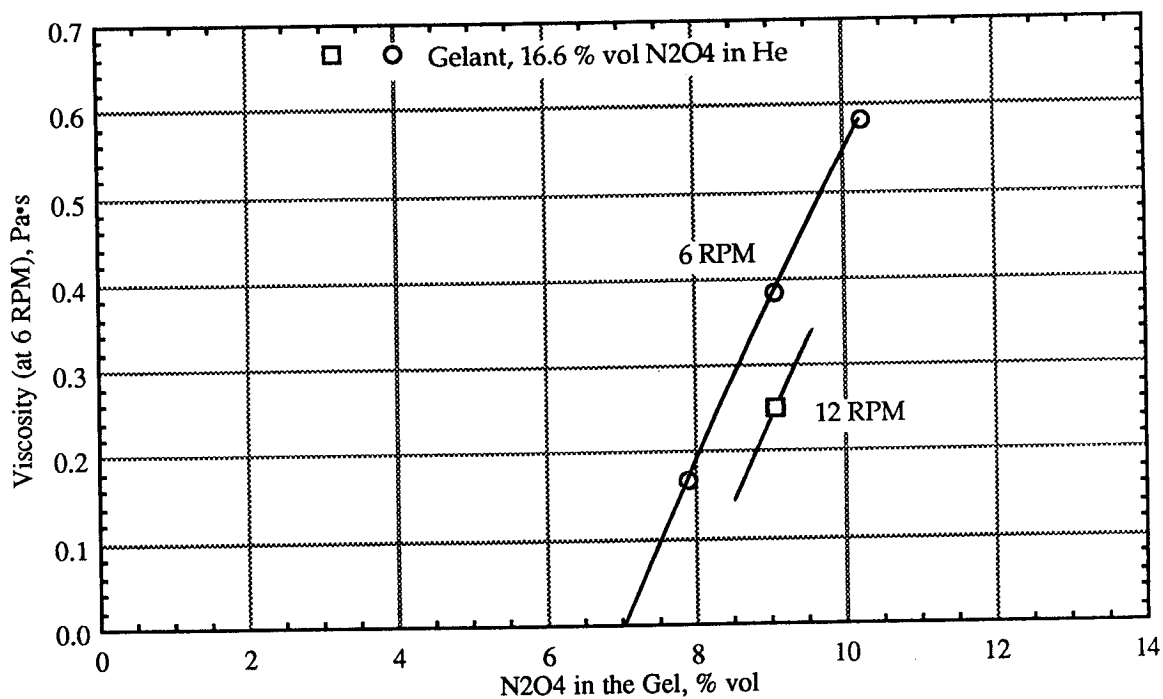


Figure 11. Effect of Nitrogen Tetroxide Concentration on the Viscosity of Liquid Oxygen Gel C-9

## C. SIMPLE LIQUID OXYGEN GELS PREPARED WITH NITROGEN TETROXIDE/OXYGEN GELANT

Two series of liquid oxygen gels were prepared using oxygen-diluted $N_2O_4$ (17.1 and 55.4 % vol $N_2O_4$, respectively) as the gelling agent. A dilute vapor-phase injection method was used in each case to introduce the gaseous gelant into the liquid oxygen.

The characteristics of these liquid oxygen/$N_2O_4$ gels are summarized in Table V. Gels containing 4.3 to 13.7 % vol (6.9 to 20.7% wt) $N_2O_4$ were studied. Neither of these series of gels (C-8 or C-6) showed tendencies to settle but the latter, which was formulated using a very $N_2O_4$-rich $N_2O_4$-$O_2$ gas mixture as a gelant, formed a gel layer and a hard sediment of agglomerated $N_2O_4$ particles (probably the result of insufficient agitation). Yield stresses of the C-8 series of gels are shown in Figure 12 as a function of $N_2O_4$ concentration. Figure 12 shows that approximately 4 % vol $N_2O_4$ is required to achieve the onset of gelation and about 7 % vol is needed to produce a gel with a yield stress of 100 Pa (1000 dynes/$cm^2$). A comparison of gel C-9 in Figure 10 with gel C-8 in Figure 12 indicates that an $N_2O_4$ -$O_2$ gelant containing about 17 %vol $N_2O_4$ is a significantly more effective gelant than an $N_2O_4$-He gelant of similar $N_2O_4$ concentration, a very important observation.

## D. SIMPLE LIQUID OXYGEN GELS PREPARED WITH Cab-O-Sil (H-5) GELANT

Two series of liquid oxygen gels were prepared using Cab-O-Sil (H-5) as the gelling agent. A high-shear mixing process was used in each case to disperse the particulate gelling agent in the liquid oxygen.

The characteristics of these liquid oxygen gels are summarized in Table VI. Gels containing 1.2 to 3.4 % vol (2.1 to 6.0% wt) Cab-O-Sil were studied. As can be seen in Table VI, only gel series C-5 exhibited tendencies to settle (i.e., formed supernatant layers upon standing for 30 min.) and such behavior occurred only at Cab-O-Sil concentrations of less than approximately 1.4 % vol. The effect of Cab-O-Sil concentration on the volume of supernatant layer and on the yield stress of the gel layer are shown in Figure 13. The supernatant layer disappeared at a Cab-O-Sil concentration of about 1.4 % vol at which point a continuous gel formed. At a Cab-O-Sil concentration of 1.9 % vol, the gel exhibited a small but measurable yield stress and a relatively strong gel (100 Pa, 1000 dynes/$cm^2$) was formed at a Cab-O-Sil concentration of approximately 2.8 % vol.

Viscosities of the C-5 series of gels were measured with a Brookfield viscometer at various shear rates (rotational speeds of 6 to 60 RPM). The viscosity values are displayed versus shear rate for several gels in Figure 14 and versus Cab-O-Sil concentration at various shear rates in Figure 15. Figure 14 demonstrates that the gels shear thin rapidly with shear rate. Figure 15 clearly shows that a Cab-O-Sil concentration greater than approximately 1.6 % vol is required to develop gel structure (as evidenced by a viscosity greater than ungelled oxygen, 2.9 x $10^{-4}$ Pa•s).

## Table V

### Characteristics of Simple Liquid Oxygen Gels Prepared with Nitrogen Tetroxide/Oxygen Gelant [1]

| Gel Identification:  C-8 | | | Gelant:  17.1 ± 1.4 % vol N2O4 in O2 | | | |
|---|---|---|---|---|---|---|
| Cryogen:  Liquid Oxygen at 77.35 K (NBP of Nitrogen) | | | | | | |
| Gelant Concentration in the Gel Layer | | Super-natant, | Gel Density [2] | | Yield Stress [3] | |
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm |
| 6.86 | 4.28 | 0.00 | 1236 | 1.236 | V. low | V. low |
| 7.90 | 4.95 | 0.00 | 1241 | 1.241 | 29.7 | 297 |
| 8.64 | 5.44 | 0.00 | 1245 | 1.245 | 28.7 | 287 |
| 9.71 | 6.14 | 0.00 | 1250 | 1.250 | 53.7 | 537 |
| 10.43 | 6.61 | 0.00 | 1254 | 1.254 | 84.2 | 842 |
| 13.00 | 8.33 | 0.00 | 1267 | 1.267 | 191.7 | 1917 |

| Gel Identification:  C-6 | | | Gelant:  55.4 ± 1.5 % vol N2O4 in O2 | | | |
|---|---|---|---|---|---|---|
| Cryogen:  Liquid Oxygen at 77.35 K (NBP of Nitrogen) | | | | | | |
| Gelant Concentration in the Gel Layer | | Super-natant, | Gel Density [2] | | Yield Stress | |
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm |
| ≈ 20.7 | ≈ 13.7 | 0.00 | 1309 | 1.309 | — | — |

[1] All gel characteristics defined at the normal boiling point (NBP) of liquid nitrogen
[2] Calculated values based on component densities (liquid oxygen = 1202.8 kg/cu m, solid nitrogen tetroxide = 1979 kg/cu m).
[3] Determined with a cone penetrometer
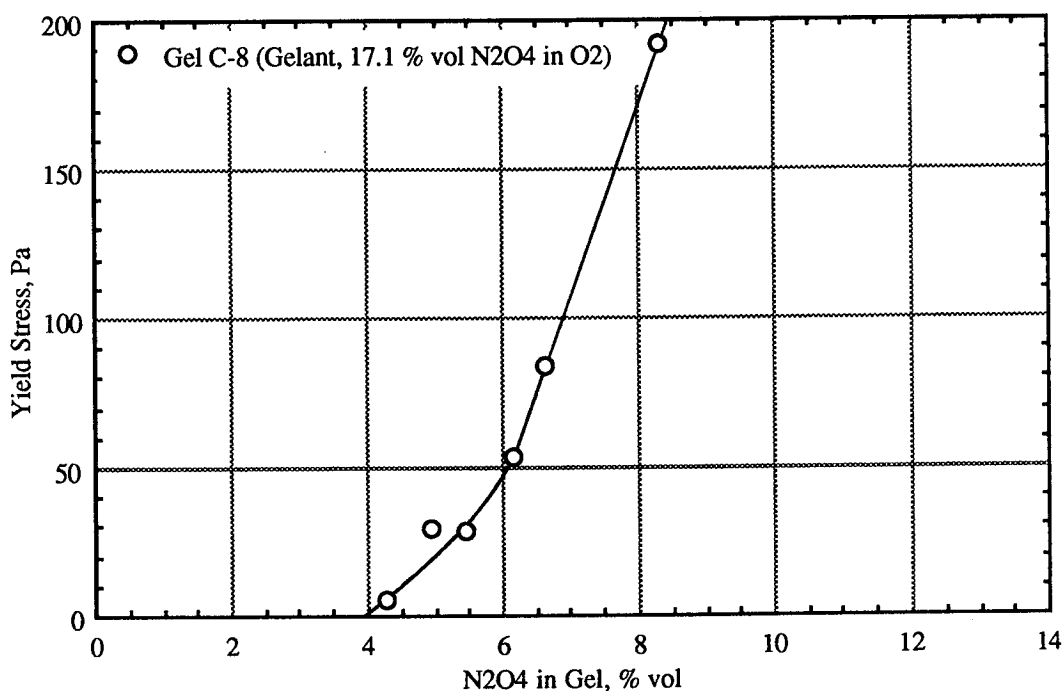


Figure 12.  Yield Stress of Liquid Oxygen Gels Prepared with Nitrogen Tetroxide-Oxygen Gelant

**Table VI**

**Characteristics of Simple Liquid Oxygen/Cab-O-Sil Gels [1]**

| Gel Identification: C-4 | | | | Gelant: Cab-O-Sil, H-5 | | | Cryogen: Liquid Oxygen at 77.35 K (NBP of Nitrogen) | | | | | | | |

| Gelant Conc. in Gel Layer | | Super-natant, | Gel Density [2] | | Yield Stress | | Viscosity, Pa·s | | | | Viscosity, centipoise | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm | 6 RPM | 12 RPM | 30 RPM | 60 RPM | 6 RPM | 12 RPM | 30 RPM | 60 RPM |
| 4.60 | 2.57 | 0 | 1228 | 1.228 | — | — | — | — | — | — | — | — | — | — |
| 5.99 | 3.37 | 0 | 1236 | 1.236 | — | — | — | — | — | — | — | — | — | — |

| Gel Identification: C-5 | | | | Gelant: Cab-O-Sil, H-5 | | | Cryogen: Liquid Oxygen at 77.35 K (NBP of Nitrogen) | | | | | | | |

| Gelant Conc. in Gel Layer | | Super-natant, | Gel Density [2] | | Yield Stress | | Viscosity, Pa·s [3] | | | | Viscosity, centipoise [3] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| % wt | % vol | % vol | kg/cu m | g/cc | Pa | dy/sq cm | 6 RPM | 12 RPM | 30 RPM | 60 RPM | 6 RPM | 12 RPM | 30 RPM | 60 RPM |
| 2.15 | 1.19 | 12.3 | 1215 | 1.215 | — | — | — | — | — | — | — | — | — | — |
| 2.33 | 1.29 | 5.56 | 1216 | 1.216 | — | — | — | — | — | — | — | — | — | — |
| 2.49 | 1.38 | 0 | 1217 | 1.217 | ≈ 0 | ≈ 0 | — | — | — | — | — | — | — | — |
| 2.82 | 1.56 | 0 | 1218 | 1.218 | ≈ 0 | ≈ 0 | — | — | — | — | — | — | — | — |
| 3.03 | 1.68 | 0 | 1220 | 1.220 | ≈ 0 | ≈ 0 | 0.050 | 0.021 | 0.010 | 0.005 | 50 | 20.8 | 10 | 5 |
| 3.45 | 1.92 | 0 | 1222 | 1.222 | 3.7 | 37 | 0.167 | 0.100 | 0.016 | 0.013 | 167 | 100 | 16 | 12.5 |
| 4.29 | 2.39 | 0 | 1227 | 1.227 | 3.4 | 34 | — | — | — | — | — | — | — | — |
| 4.94 | 2.76 | 0 | 1230 | 1.230 | 54.6 | 546 | 0.283 | 0.200 | 0.110 | 0.037 | 283 | 200 | 110 | 37 |
| 5.34 | 2.99 | 0 | 1233 | 1.233 | 222 | 2224 | >1.67 | — | — | — | >1667 | — | — | — |

[1] All gel characteristics defined at the normal boiling point (NBP) of liquid nitrogen
[2] Calculated values based on component densities (liquid oxygen = 1202.8 kg/cu m, Cab-O-Sil = 2200 kg/cu m)
[3] Determined with a Brookfield viscometer
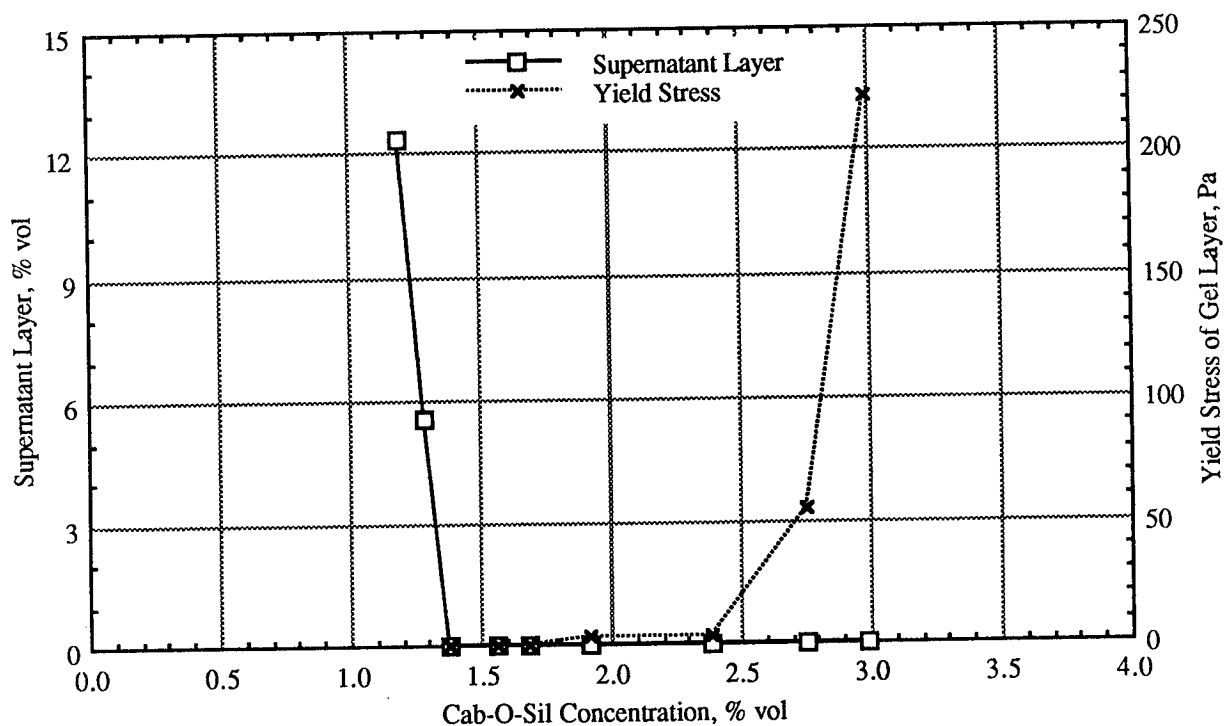


**Figure 13. Effect of Cab-O-Sil Concentration on Supernatant Layer Volume and Gel Layer Yield Stress**
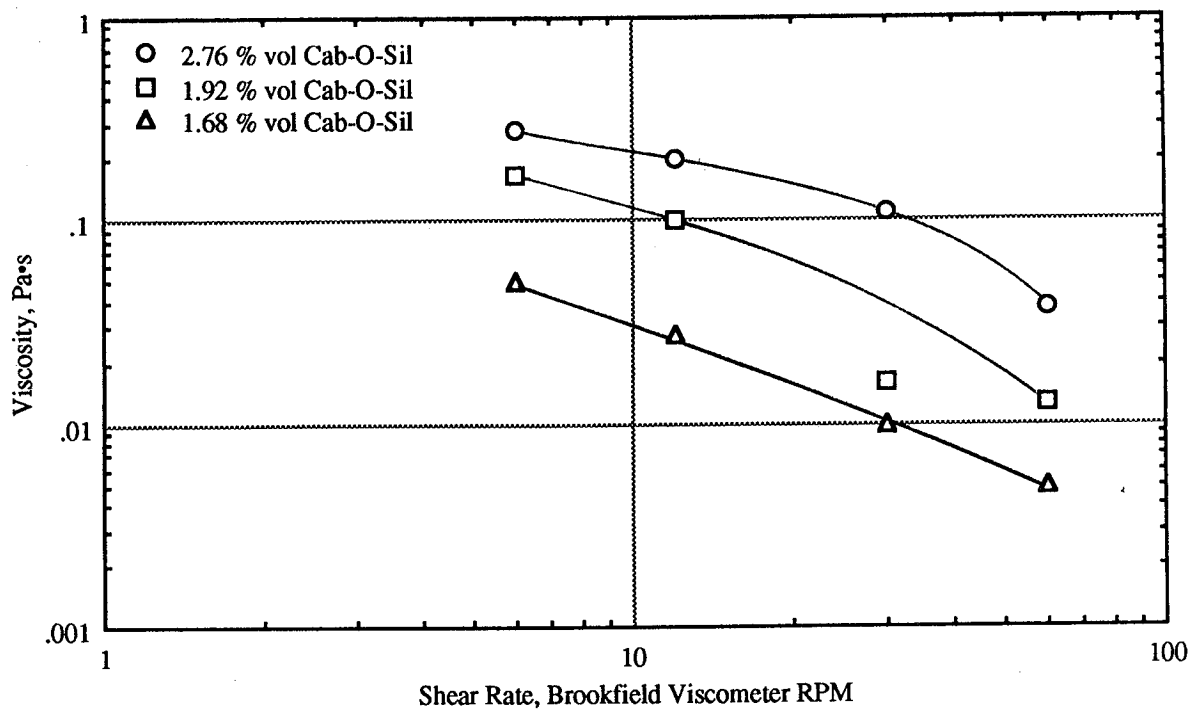
Figure 14. Effect of Shear Rate on the Viscosity of Simple Liquid Oxygen/Cab-O-Sil Gels
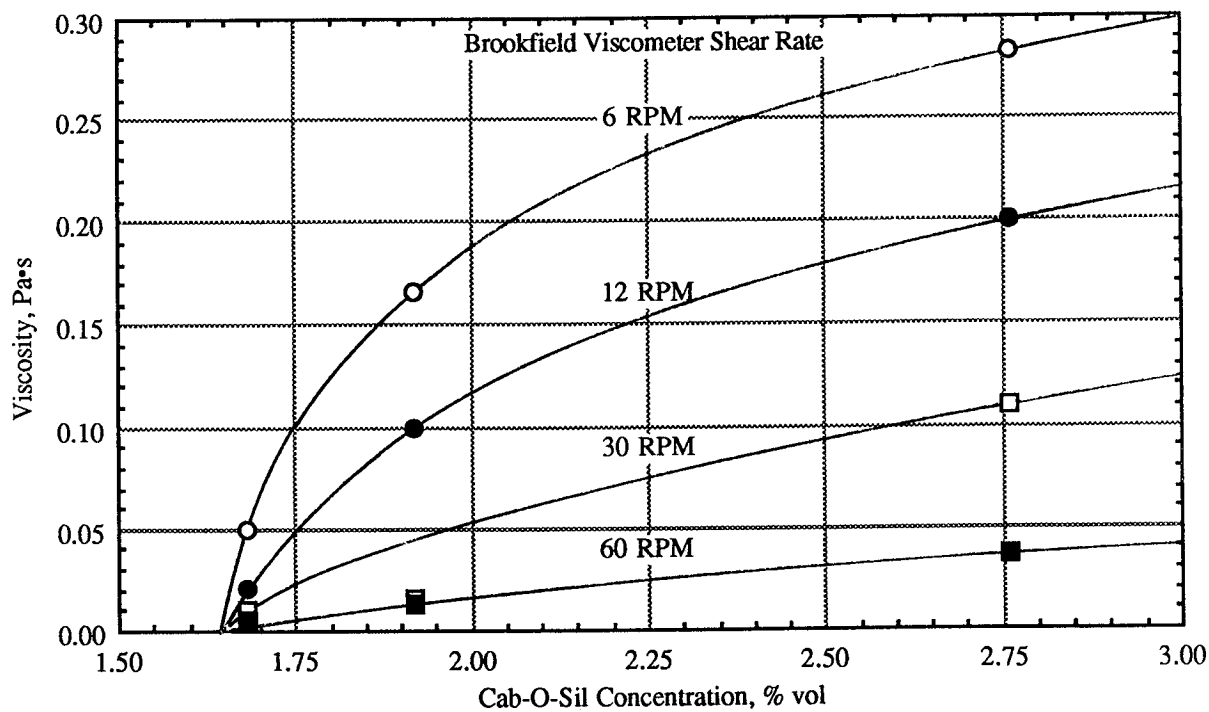


Figure 15. Effect of Cab-O-Sil Concentration on the Viscosity
of Simple Liquid Oxygen/Cab-O-Sil Gels

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## E. SUMMARY OF ACCOMPLISHMENTS

Four types of simple cryogenic gels were prepared and evaluated under Task III. Initial effort involved the preparation of liquid nitrogen gels using $N_2O_4$ as the gelling agent and a dilute vapor-phase injection method for introducing the gelling agent into the cryogen. The initial work served as a checkout of the test equipment and a first proof-of-principle demonstration that minute $N_2O_4$ particles will gel a nonpolar cryogen. Subsequently, two types of liquid oxygen gels were similarly prepared using $N_2O_4$ diluted with helium and with gaseous oxygen, respectively, as gelling agents. Liquid oxygen gels containing 3 to 33 % vol (4 to 45 % wt) $N_2O_4$ were evaluated in regard to physical stability, structure, and rheological behavior. Liquid oxygen gels were also prepared using Cab-O-Sil (H-5) as the gelling agent and a simple high-shear mixing technique to disperse it in the liquid oxygen. Liquid oxygen gels containing 1.1-3.4 % vol (1.9-6.0 % wt) Cab-O-Sil (H-5) were evaluated in respect to physical stability, structure, and rheological behavior. The two apparatuses used to prepare cryogenic gels formed with $N_2O_4$ /carrier gases and with Cab-O-Sil (H-5) are shown schematically in Figure 7 and 8.

## V. FORMULATION AND EVALUATION OF HETEROGENEOUS GELS

The research performed under Task IV was comprised of two parts. The first effort was directed toward preparing fine particles of solid $N_2O_4$ and evaluating their characteristics. The second part of the task involved formulating and evaluating heterogeneous gels comprised of solid $N_2O_4$ particles suspended in gelled liquid oxygen. This research is summarized in the following sections.

### A. PREPARATION AND EVALUATION OF FINE PARTICLES OF SOLID NITROGEN TETROXIDE ($N_2O_4$)

Two basic approaches to preparing fine particles of $N_2O_4$ were pursued: (1) subsurface injection of gaseous $N_2O_4$ mixtures into liquid nitrogen or liquid oxygen and (2) injection of liquid $N_2O_4$ onto the surface of liquid nitrogen or oxygen. The results achieved with each of these approaches are summarized in the following subsections.

# 1. Solid Nitrogen Tetroxide Particles from Subsurface Injection of Gaseous Nitrogen Tetroxide Mixtures

Much of this research was done in conjunction with that performed under Task III on the formulation and evaluation of simple cryogenic gels. Solid $N_2O_4$ particles were prepared by injecting various gaseous mixtures of $N_2O_4$ and helium or $N_2O_4$ and oxygen (3.6 to 55.4 % vol $N_2O_4$) into liquid nitrogen or liquid oxygen using the vacuum-jacketed, internally heated injection tubes shown in Figure 6. These special injection tubes were submerged below the surface of the cryogens to a depth of approximately 25 cm (10 in.) and operated at a pressure of 0.308 MPa (30 psig). The gas mixtures were injected into the cryogens via a single orifice either 0.51 or 0.64 mm (0.020 or 0.025 in.) in dia. All test operating conditions and the corresponding test results are summarized in Table VII and Figure 16.

Particles of $N_2O_4$ formed from the very dilute $N_2O_4$ gas mixtures, i.e., those containing 3.6 to 7.9 % vol $N_2O_4$, were too small to determine their sizes from observations with an optical microscope or from sedimentation studies. These particles appeared to form flocs and remained suspended in the cryogens for periods in excess of the nominal 1-hr observation times. Such low settling rates, i.e., $\leq 1 \times 10^{-4}$ cm/s, suggest that the particles had equivalent sphere diameters of < 1 μm (see Appendix B). The yields of particles from the $N_2O_4$ gas mixtures were 55.4 and 60.6 % wt from mixtures containing 4.4 and 7.9 % vol $N_2O_4$, respectively.

Particles formed from gas mixtures containing approximately 17 % vol $N_2O_4$ ranged in size from 1 to 200 μm but were mostly in the 1 to 4 μm range. The larger particles appeared to be agglomerates of much smaller individuals. Sedimentation evaluations in liquid oxygen on drops of oxygen gel formed by such particles gave settling rates indicative of agglomerated particles having equivalent sphere diameters of about 42 μm. Dilute suspensions of particles formed from the $N_2O_4$-$O_2$ gas mixture did not settle and form a distinct layer whereas those formed from the $N_2O_4$-He mixture did settle and form a distinct layer containing about 6.9 % vol of solid $N_2O_4$. The particles formed from the $N_2O_4$-$O_2$ and $N_2O_4$-He gas mixtures produced oxygen gels having yield stresses of about 100 Pa (1000 dynes/cm$^2$) at solid $N_2O_4$ concentrations of 7.0 and 10.0 % vol, respectively. The yields of particles from the $N_2O_4$ gas mixtures were 64.4 and 66.8 % wt from mixtures containing 16.6 and 17.1 % vol $N_2O_4$, respectively.

Particles formed from a $N_2O_4$-He mixture containing 48.4 % vol $N_2O_4$ ranged in size from 4 to 200 μm, but were mostly in the 4 to 15 μm range. Again, the larger particles appeared to be agglomerates of much smaller individuals. Sedimentation evaluations in liquid oxygen on drops of oxygen gel formed by such particles gave settling rates indicative of agglomerated particles having equivalent sphere diameters of about 46 μm. Suspensions of particles formed from this $N_2O_4$-He gas mixture settled and produced a distinct layer containing about 7.1 % vol of solid $N_2O_4$. At a particle concentration corresponding to 11.7 % vol of solid $N_2O_4$, a gel with a yield stress of about 100 Pa (1000

## Table VII

### Characteristics of Solid Nitrogen Tetroxide Particles Formed by Vapor-Phase Injection Process

| Pressure, MPa (psig) | Sub. Depth, cm (in) | Orif. Dia. mm (in) | N2O4, % vol | Diluent Gas | Liquid Cryogen Used | Particle Size, µm by Sed. [1] | Optical [2] | Particle Descript. | % vol in setl'd layer | % vol to form gel [3] | Particle Yield, % wt [4] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.308 (30) | ≈ 25 (≈ 10) | 0.51 (0.020) | 3.6 | Helium | Nitrogen | — | — | Flocculent | No layer | ≈ 8 | — |
| 0.308 (30) | ≈ 25 (≈ 10) | 0.64 (0.025) | 4.2 | Helium | Oxygen | — | — | Flocculent | No layer | ≈ 10 | — |
| 0.308 (30) | ≈ 25 (≈ 10) | 0.51 (0.020) | 4.4 | Helium | Oxygen | — | — | Flocculent | No layer | ≈ 8.5 | 55.4 |
| 0.308 (30) | ≈ 25 (≈ 10) | 0.51 (0.020) | 7.9 | Helium | Nitrogen | — | — | Flocculent | No layer | ≈ 10 | 60.6 |
| 0.308 (30) | ≈ 25 (≈ 10) | 0.64 (0.025) | 16.6 | Helium | Oxygen | — | 1 - 200 | [5] | 6.9 | 10.0 | 64.4 |
| 0.308 (30) | ≈ 25 (≈ 10) | 0.64 (0.025) | 17.1 | Oxygen | Oxygen | 42 ± 2 | — | — | No layer | 7.0 | 66.8 |
| 0.308 (30) | ≈ 25 (≈ 10) | 0.64 (0.025) | 48.4 | Helium | Oxygen | 46 ± 3 | 4 - 200 | [6] | 7.1 | 11.7 | 80.0 |
| 0.308 (30) | ≈ 25 (≈ 10) | 0.64 (0.025) | 55.4 | Oxygen | Oxygen | 30 - 54 | 10 - 30 | [7] | — | ≈ 14 | — |

[1] Determined from the settling velocities in liquid oxygen (at NBP of N2) of the bulk of the particles
[2] Determined by observations using an optical microscope
[3] Concentration of solid N2O4 particles necessary to form a gel with a yield stress of approximately 100 Pa
[4] Percent of N2O4 injected which was captured as particles
[5] Mostly 1-4 µm spheres, larger particles appeared to be agglomerates
[6] Mostly 4-15 µm spheres, larger particles appeared to be agglomerates
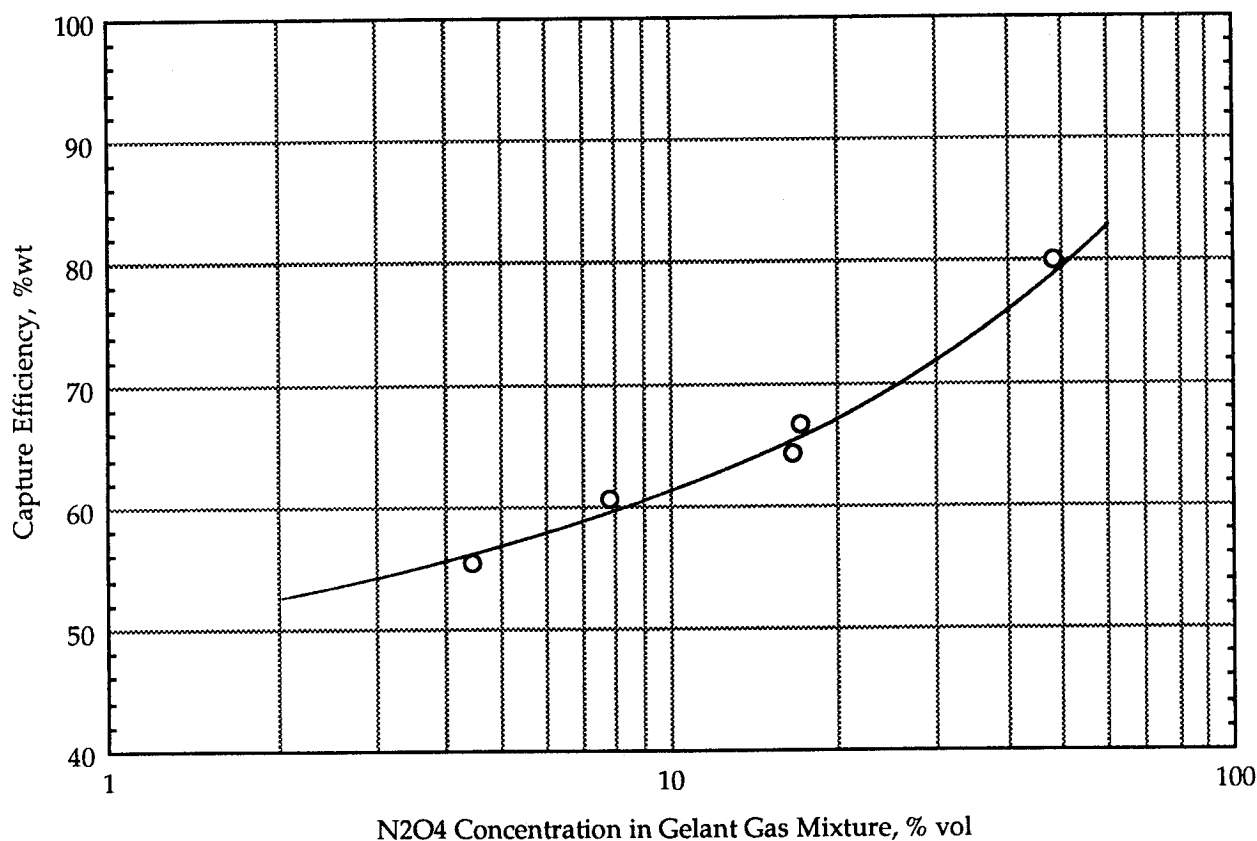[7] Much of the particulate N2O4 agglomerated into a large solid mass



Figure 16. Capture Efficiencies of Nitrogen Tetroxide in Liquid Nitrogen or Oxygen from Gas Mixtures

dynes/cm$^2$) was produced. The yield of particles from the N$_2$O$_4$-He gas mixture containing 48.4 % vol N$_2$O$_4$ was 80.0 % wt.

Solid N$_2$O$_4$ formed from an N$_2$O$_4$-O$_2$ mixture containing 55.4 % vol N$_2$O$_4$ produced a complex system composed of a weak oxygen gel layer above a large solid mass of agglomerated particles. Inspection of the N$_2$O$_4$ particles in the gel layer with an optical microscope indicated most of the particles to be the range of 10 to 30 μm. Sedimentation evaluations in liquid oxygen on drops of the gel layer gave settling rates indicative of agglomerated particles having equivalent sphere diameters in the range of 30 to 54 μm. Particles of the nature observed in the gel layer could be expected to form a gel with a yield stress of about 100 Pa (1000 dynes/cm$^2$) at a concentration corresponding to about 14 % vol of solid N$_2$O$_4$.

The particle yields or efficiencies at which N$_2$O$_4$ is captured as particles from the subsurface injection of the various N$_2$O$_4$-gas mixtures are shown in Figure 16 as a function of N$_2$O$_4$ concentration in the gas mixture.

## 2. Solid Nitrogen Tetroxide Particles from the Surface Injection of Liquid Nitrogen Tetroxide

Solid N$_2$O$_4$ particles were prepared by injecting liquid N$_2$O$_4$ onto the surfaces of liquid nitrogen and liquid oxygen via a single small orifice directed normal to the liquid surface. The injector was operated at pressures ranging from slightly above 0.101 to about 0.515 MPa (0 to 60 psig) but was most often operated at 0.38 MPa (40 psig). It was positioned roughly 10 cm (4 in.) above the surface of the cryogen but varied from that height by perhaps ± 5 cm (2 in.) in some instances. The injector orifice diameter was 0.114 mm (0.0045 in.) except in a single experiment in which case a 0.53 mm (0.021 in.) orifice was used. The temperature of the N$_2$O$_4$ supplied to the injector varied from 273 K (32 °F) to slightly greater than 294 K (70 °F), its normal boiling point. Thus, the N$_2$O$_4$ issuing from the orifice was a subcooled liquid in most experiments and a flashing liquid in a few experiments. These streams of N$_2$O$_4$ droplets (and vapor) were impinged upon various liquid cryogenic surfaces including: (1) slowly boiling nitrogen, (2) slowly boiling oxygen, and (3) stirred liquid oxygen cooled by a liquid nitrogen bath. All test operating conditions and the corresponding test results are summarized in Table VIII.

The first group of tests listed in Table VIII involved the injection of slightly subcooled N$_2$O$_4$ at modest pressures through a single small orifice onto a calm surface of liquid nitrogen or liquid oxygen. Based on observations with an optical microscope, the N$_2$O$_4$ particles ranged in size from about 4 to 360 μm in dia. and were mostly less than 60 μm. Many of the larger particles appeared to be agglomerates of smaller individuals. In a sedimentation test in liquid oxygen, the bulk of a sample of particles settled at rates indicative of diameters of 300 ± 100 μm. This also suggests that considerable particle agglomeration occurred. The particles were generally pale yellow or cream colored spheres. However, the smaller ones observed in the test involving injection onto an oxygen surface appeared to be

### Table VIII

### Characteristics of Solid Nitrogen Tetroxide Particles Formed by Liquid-Phase Injection Process

| Injector Operating Conditions | | | N2O4 Temp., K (°F) | Liquid Cryogen | | Solid N2O4 Particle Characteristics | | | | | Particle Yield, % wt [5] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Pressure, MPa (psig) | Height, cm (in) [1] | Orif. Dia. μm (in) | | Type Used | Dynamic State | Particle Size, μm by Sed. [2] | Optical [3] | Particle Descript. | % vol in setl'd layer | % vol to form gel [4] | |
| ≤0.31 (≤30) | 12.1 (4.75) | 114 (0.0045) | 291 (64) | Nitrogen | Calm [6] | 300 ± 100 | 4 - 160 | [7] | — | — | — |
| 0.38 (40) | 11.4 (4.5) | 114 (0.0045) | 291 (64) | Nitrogen | Calm [6] | — | 4 - 360 | [8] | ≈ 61 | — | — |
| 0.38 (40) | 11.4 (4.5) | 114 (0.0045) | 291 (64) | Oxygen | Calm [6] | — | 4 - 360 | [9] | ≈ 56 | — | — |
| 0.38 (40) | ≈ 10 (≈ 4) | 114 (0.0045) | [10] | Oxygen | Stirred | — | — | [11] | 64.6 | < 65.7 | ≈ 74 |
| 0.515 (60) | ≈ 10 (≈ 4) | 114 (0.0045) | 273 (32) | Oxygen | Stirred | — | 4 - 200 | [12] | ≈ 58 | ≈ 60 | ≈ 67 |
| 0.38 (40) | ≈ 10 (≈ 4) | 114 (0.0045) | [13] | Oxygen | Stirred | — | — | [11] | ≈ 20 | — | — |
| 0.24-0.38 (20-40) | ≈ 10 (≈ 4) | 530 (0.021) | [13] | Oxygen | Stirred | — | 4 - 50 | — | 26.8 | — | ≈ 28 |

[1] Nominal distance above the surface of the cryogen
[2] Determined from the settling velocities in liquid oxygen (at NBP of N2) of the bulk of the particles
[3] Determined by observations using an optical microscope
[4] Concentration of solid N2O4 particles necessary to form a gel with a yield stress of approximately 100 Pa
[5] Percent of N2O4 injected which was captured as particles
[6] Unstirred, very slowly boiling liquid contained in a Dewar
[7] Spherical particles, pale yellow in color, large number of particles in the range of 40 to 160 μm
[8] Spherical particles, pale yellow in color, many particles in the range of 4 to 40 μm
[9] Cream colored, many particles in the range of 4 to 60 μm, smallest appear irregular shaped, larger are spherical
[10] Not measured but apparently < 294 K (70°F) as evidenced by little or no flashing at or near the injection orifice
[11] Creamy-white particles
[12] Very white particles
[13] Not measured but apparently > 294 K (70°F) as evidenced by flashing behavior at or near the injection orifice

somewhat less regular in shape than those formed in nitrogen. Settled layers of these solid particles in liquid nitrogen and liquid oxygen contained approximately 61 and 56 % vol N2O4, respectively. These relatively high volumetric loadings are consistent with that normally observed in slurries of spheroidal particles and the lower value (i.e., the 56 % vol loading) is indicative of more irregular particles.

The second group of two tests listed in Table VIII involved the injection of subcooled N2O4 at modest pressures through a single small orifice onto an agitated surface of liquid oxygen. The results of this second group of tests were generally similar to those of the first. The two tests differed from one another primarily in regard to injector operating pressure and the degree of subcooling of the injected N2O4. The second of the two tests utilized a higher injection pressure (0.515 versus 0.38 MPa) and colder N2O4 (273 versus < 294 K). Particle sizes ranged from approximately 4 to 200 μm in dia. in the experiment involving the higher injection pressure and colder N2O4. These injection conditions also appeared to alter other particle characteristics slightly from those observed under normal injection conditions. For example, the particles exhibited a lighter or whiter color, their concentration or volumetric loading in a settled layer was somewhat lower (≈ 58 versus 64.6 % vol), the concentration of

particles necessary to form a gel was lower ($\approx$ 60 versus < 65.7 % vol), and the particle yield was lower ($\approx$ 67 versus $\approx$ 74 % vol).

The third group of tests listed in Table VIII involved the injection of flashing rather than subcooled $N_2O_4$ at modest pressures through single orifices of different diameters onto the surface of agitated liquid oxygen . The results of this group of tests differed substantially from those of the other groups of tests in several aspects. First, the upper particle size was smaller, i.e., about 50 versus 160 to 360 $\mu$m. This is consistent with the fact that pressure nozzles produce smaller droplets from flashing liquids than from subcooled liquids. Second, the volumetric concentration of particles in settled layers was much lower for flashing $N_2O_4$ than for subcooled $N_2O_4$ ($\approx$ 20 to 27 versus 56 to 65 % vol). Such low concentrations are also indicative of smaller particle sizes. Finally, the yield of particles was much lower for flashing $N_2O_4$ than for subcooled $N_2O_4$ ($\approx$ 28 versus 67 to 74 % vol). A comparison of the two tests within the third group with one another shows that the larger nozzle orifice produced a higher volumetric concentration of particles in the settled layer than did the small orifice. This also indicates the smaller orifice produced smaller droplets and particles than the larger orifice and is consistent with expectations.

### 3. Comparison of Solid Nitrogen Tetroxide Particles from the Two Processes

The two different processes for preparing solid $N_2O_4$ particles (i.e., subsurface injection of gaseous $N_2O_4$ mixtures and surface injection of liquid $N_2O_4$ into or onto cryogenic liquids) yield particles with distinctly different characteristics. The former process generally produces very small particles (equal to or less than a few microns) which have either (1) little tendency to settle or (2) form layers that contain relatively small concentrations of solid $N_2O_4$. Such particles are desirable and useful for producing fluids with structure (i.e., effective gelling agents) but, to achieve acceptable rheological properties, their concentrations are limited to relatively low values (probably less than 15 % vol). Thus, $N_2O_4$ particles formed by the subsurface vapor injection process are primarily useful as gelants but undesirable for achieving heterogeneous gels with high volumetric loadings of solid $N_2O_4$ particles.

The injection of liquid $N_2O_4$ onto a cryogen surface may, on the other hand, yield either moderate sized particles (e.g., 4 to 50 $\mu$m in dia.) or considerably larger particles (e.g., 4 to 360 $\mu$m in dia.) depending upon whether the liquid is above its boiling point (flashing) or is subcooled. The latter, larger particles can be present in the cryogen at volumetric loadings on the order of 55 to 65 % vol without producing significant structure other than that common to highly loaded slurries. Thus, such particles are very useful for formulating highly loaded heterogeneous gels. The intermediate sized particles produced from flashing $N_2O_4$ appear to be most useful in preparing heterogeneous gels with intermediate loadings of $N_2O_4$ in liquid oxygen (i.e., $\approx$ 15 to 45 % vol).

# B. PREPARATION AND EVALUATION OF HETEROGENEOUS GELS

Three types of heterogeneous liquid oxygen-solid $N_2O_4$ systems were prepared and evaluated: (1) simple settled slurries, (2) thickened slurries, and (3) gels. Simple settled slurries and thickened slurries were evaluated to define the approximate upper loading limits for various types and sizes of $N_2O_4$ particles that are possible in ungelled liquid oxygen-solid $N_2O_4$ systems. Both of those studies provided valuable insights into the compositions and apparatus operating conditions necessary to prepare the desired gel systems. The preparation and evaluation of each of these types of systems is described in the following subsections.

## 1. Settled Slurries of Solid Nitrogen Tetroxide in Liquid Oxygen

Settled slurries were prepared by the *in situ* formation of solid $N_2O_4$ particles in liquid oxygen (cooled in a liquid nitrogen bath). The particles were generated by the subsurface vapor phase injection and/or liquid phase surface injection methods described in earlier sections. The former approach produced very small particles with generally good gelling capabilities which are, thus, referred to here as "$N_2O_4$ gelant". The latter approach produced larger particles with little or no gelling capabilities and are referred to here simply as "$N_2O_4$ particles" when differentiation between particle types is necessary for clarity. Settled slurries were prepared by allowing suspensions of either or both of these types of $N_2O_4$ particles to settle for approximately one hour to define the interface between the settled slurry and the supernatant liquid oxygen layers. Normally, the supernatant oxygen layer was then removed by sparging with helium until the volume of the preparation was reduced to that of the observed settled slurry layer. A sample was placed in a small Dewar and gravimetrically analyzed for $N_2O_4$ by allowing the remaining oxygen to evaporate slowly, leaving the solid $N_2O_4$ behind. This defined the mass compositions of the settled slurries. The densities of both solid $N_2O_4$ and liquid oxygen are well established (see Appendix A), permitting the volumetric compositions and bulk densities to be calculated. In cases where both types of particles were present, the portion of each type was defined from knowledge of the total quantity of particles produced, the amount of $N_2O_4$ used to prepare $N_2O_4$ gelant, and particle yields from the injection process (see Figure 16).

A number of settled slurries were prepared and evaluated. The operating conditions employed in preparing the particles and the characteristics of the corresponding settled slurries are summarized in the upper portions of Table IX. The slurries in the uppermost portion of Table IX contained only the larger "$N_2O_4$ particles" whereas those in the second portion of the table contained both types of particles. The slurries in the third part of the table contained only "$N_2O_4$ gelant" particles. None of these preparations possessed any significant structure and, therefore, each is indicated to have a yield stress of approximately zero. Focusing on the uppermost part of Table IX, it can be seen that two of the

**Table IX**

**Characteristics of Settled and Thickened Slurries of Solid Nitrogen Tetroxide in Liquid Oxygen**

| Oper. Cond. for the Prep. of N2O4 Gelant and Particles | | | | | Characteristics of Settled Slurries of Solid N2O4 Particles in Liquid Oxygen | | | | | |
| N2O4 Gelant | | N2O4 Particles | | | Yield Stress, Pa | Composition, % vol. | | | | Density, kg/cu m [2] |
| N2O4 Conc., % vol [1] | Gas Mixture Diluent | N2O4 Temp., K (°F) | Injector Conditions | | | N2O4 Gelant | N2O4 Particles | Total N2O4 | Liquid Oxygen | |
| | | | Pressure, MPa (psig) | Orif. Dia., μm (in.) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **Settled Slurries** | | | | | |
| — | — | [3] | 0.38 (40) | 114 (0.0045) | ≈0 | 0 | ≈20 | ≈20 | ≈80 | ≈1307 |
| — | — | [3] | [4] | 530 (0.021) | ≈0 | 0 | 26.8 | 26.8 | 73.2 | 1364 |
| — | — | 273 (32) | 0.515 (60) | 114 (0.0045) | ≈0 | 0 | 57.9 | 57.9 | 42.1 | 1622 |
| — | — | <294 (<70) | 0.38 (40) | 114 (0.0045) | ≈0 | 0 | 64.6 | 64.6 | 35.4 | 1678 |
| 4.3 | Helium | [3] | 0.38 (40) | 114 (0.0045) | ≈0 | 3.0 | 7.3 | 10.3 | 89.7 | 1227 |
| 17.6 | Helium | [3] | 0.38 (40) | 114 (0.0045) | ≈0 | ≈9.0 | ≈22.6 | ≈31.6 | ≈68.4 | ≈1403 |
| 16.6 | Helium | — | — | — | ≈0 | 6.9 | — | 6.9 | 93.1 | 1198 |
| 48.4 | Helium | — | — | — | ≈0 | 7.1 | — | 7.1 | 92.9 | 1200 |
| | | | | | **Thickened Slurries** | | | | | |
| — | — | [3] | [4] | 530 (0.021) | [5] | 0 | 27.9 | 27.9 | 72.1 | 1373 |
| — | — | <294 (<70) | 0.38 (40) | 114 (0.0045) | [6] | 0 | 65.7 | 65.7 | 34.3 | 1687 |

[1] Concentration of N2O4 in the gas mixture used to prepare the N2O4 gelant particles
[2] Calculated values at the NBP of oxygen (90.18 K) based on solid N2O4 and LOX densities of 1971.6 and 1141.0 kg/cu m, respectively
[3] Not precisely defined but considerable flashing observed at the injector indicated a temperature > 294 K (70 °F)
[4] Variable from 0.24 to 0.38 MPa (20 to 40 psig)
[5] Not defined but characterized as a moderately thick slurry
[6] Not defined but characterized as a very thick slurry

preparations had relatively low loadings of N₂O₄ particles and two had relatively high loadings. The preparations differed mainly in the temperature of the N₂O₄ injected onto the liquid oxygen surface. The low loadings were associated with warm N₂O₄ which partially flashed upon injection, whereas the high loadings were associated with the use of subcooled N₂O₄. As discussed in a preceding section, this had a significant effect on particle sizes. Flashing N₂O₄ produced smaller particles and lower loadings than the subcooled N₂O₄. The second part of Table IX covers two preparations which contained both "N₂O₄ gelant" and N₂O₄ particles. Both of these involved the use of flashing N₂O₄ and resulted in very low or relatively low total loadings of N₂O₄. The third part of Table IX shows that the preparations containing only "N₂O₄ gelant" particles exhibited very low loadings of N₂O₄. All these preparations clearly point to the use of surface injected subcooled N₂O₄ as a preferred approach to achieve highly loaded liquid oxygen-solid N₂O₄ systems.

## 2. Thickened Slurries of Solid Nitrogen Tetroxide in Liquid Oxygen

Two thickened slurries of solid N₂O₄ in liquid oxygen were prepared, each containing only the larger type of N₂O₄ particles formed by the injection of liquid N₂O₄ onto the surface of liquid oxygen.

They were prepared and evaluated in a manner similar to that described above for the settled slurries except the sparging operation to remove excess oxygen was continued until the slurries exhibited definite structure. The operating conditions employed in preparing the particles and the characteristics of the corresponding thickened slurries are summarized in the bottom portion of Table IX. Again, the slurry prepared using $N_2O_4$ in a flashing condition upon injection resulted in a low loading of $N_2O_4$ whereas the one produced with subcooled $N_2O_4$ yielded a highly loaded slurry. The latter slurry indicates that the preparation of solid $N_2O_4$-liquid oxygen gels containing up to about 65 % vol $N_2O_4$ is feasible. It is worth noting that such a loading is close to the theoretical limit for monodisperse spherical particles.

### 3. Heterogeneous Gels of Solid Nitrogen Tetroxide in Liquid Oxygen

Fourteen heterogeneous gels of solid $N_2O_4$ in liquid oxygen were prepared using "$N_2O_4$ gelant" (i.e., very small $N_2O_4$ particles formed by subsurface injection of $N_2O_4$ gas mixtures into liquid oxygen). Even though Cab-O-Sil was demonstrated in earlier tests to be an effective gelant for liquid oxygen (see Section IV.D.), it was not used in any of these preparations because of its degrading effect on propellant performance and the fact that it would leave an undesirable solid residue upon evaporation of the gel. These gels were prepared and evaluated in much the same manner as described above for the settled slurries  The overall preparation involved three main steps:  (1) when applicable, the formation of a suspension of $N_2O_4$ particles in liquid oxygen stirred with a dual turbine mixer, (2) *in situ* preparation of "$N_2O_4$ gelant" within the suspension of $N_2O_4$ particles in liquid oxygen, and (3) sparging of the mixture with helium to remove excess oxygen and provide agitation for maintaining a uniform dispersion. The resulting gels were evaluated in the same manner as the slurries. In addition, they were characterized in respect to their yield stresses as described in Section III.C.4.

The operating conditions employed in preparing the particles and the characteristics of the corresponding heterogeneous gels are summarized in Table X. The gels listed in the upper portion of the table contained only "$N_2O_4$ gelant". These gels consistently contained low loadings of $N_2O_4$ (i.e., 6.1 to 13.0 % vol) even though the operating conditions for preparing the "$N_2O_4$ gelant" were varied significantly and the gels exhibited a wide range of yield stresses i.e., < 10 to 259 Pa (< 100 to 2590 dynes/cm$^2$). These data suggest that gels formed only from "$N_2O_4$ gelant" would become too thick for practical use at concentrations above about 15 % vol.

The first five gels listed in the lower part of Table X all contained $N_2O_4$ particles formed from flashing $N_2O_4$ which tends to produce relatively small particles. The first two of these preparations contained gelant formed from a very dilute $N_2O_4$ gas mixture (4.3 % vol in helium) whereas the latter three contained gelant formed from a more concentrated $N_2O_4$ gas mixture (17.6 % vol in helium). The first two gels exhibited yield stresses of < 10 and 23 Pa (< 100 to 230 dynes/cm$^2$) at total $N_2O_4$

## Table X

### Characteristics of Heterogeneous Liquid Oxygen-Nitrogen Tetroxide Gels

| Oper. Cond. for the Prep. of N2O4 Gelant and Particles | | | | | Characteristics of Heterogeneous Liquid Oxygen-N2O4 Gels and Slurries | | | | | |
| N2O4 Gelant | | N2O4 Particles | | | | Composition, % vol. | | | | Density, |
| N2O4 Conc., % vol [1] | Gas Mixture Diluent | N2O4 Temp., K (°F) | Injector Conditions | | Yield Stress, Pa [2] | N2O4 Gelant | N2O4 Particles | Total N2O4 | Liquid Oxygen | kg/cu m [3] |
| | | | Pressure, MPa (psig) | Orif. Dia., μm (in.) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 4.2 | Helium | — | — | — | < 10 | 9.6 | — | 9.6 | 90.4 | 1221 |
| 16.6 | Helium | — | — | — | 133 | 10.2 | — | 10.2 | 89.8 | 1226 |
| 16.6 | Helium | — | — | — | 254 | 13.0 | — | 13.0 | 87.0 | 1249 |
| 17.1 | Oxygen | — | — | — | 54 | 6.1 | — | 6.1 | 93.9 | 1192 |
| 17.1 | Oxygen | — | — | — | 192 | 8.3 | — | 8.3 | 91.7 | 1210 |
| 48.4 | Helium | — | — | — | 45 | 10.3 | — | 10.3 | 89.7 | 1227 |
| 48.4 | Helium | — | — | — | 259 | 12.4 | — | 12.4 | 87.6 | 1244 |
| 4.3 | Helium | [4] | 0.38 (40) | 114 (0.0045) | < 10 | 3.3 | 8.1 | 11.4 | 88.6 | 1236 |
| 4.3 | Helium | [4] | 0.38 (40) | 114 (0.0045) | 23 | 6.6 | 16.4 | 23.0 | 77.0 | 1332 |
| 17.6 | Helium | [4] | 0.38 (40) | 114 (0.0045) | < 10 | 9.6 | 24.1 | 33.7 | 66.3 | 1421 |
| 17.6 | Helium | [4] | 0.38 (40) | 114 (0.0045) | 19 | 11.4 | 28.7 | 40.1 | 59.9 | 1474 |
| 17.6 | Helium | [4] | 0.38 (40) | 114 (0.0045) | 154 | 13.0 | 32.6 | 45.6 | 54.4 | 1520 |
| 4.1 | Helium | 273 (32) | 0.515 (60) | 114 (0.0045) | 43 | 2.6 | 57.3 | 59.9 | 40.1 | 1639 |
| 4.1 | Helium | 273 (32) | 0.515 (60) | 114 (0.0045) | 1470 | 2.9 | 64.5 | 67.4 | 32.6 | 1701 |

[1] Concentration of N2O4 in the gas mixture used to prepare the N2O4 gelant particles
[2] Determined with a cone penetrometer.
[3] Calculated values at the NBP of oxygen (90.18 K) based on solid N2O4 and LOX densities of 1971.6 and 1141.0 kg/cu m, respectively
[4] Not precisely defined but considerable flashing observed at the injector indicated a temperature > 294 K (70 °F)

concentrations of 11.4 and 23.0 % vol, respectively. These data suggest that gels formed under these conditions and at similar ratios of $N_2O_4$ gelant to $N_2O_4$ particles would become too thick for practical use at total $N_2O_4$ concentrations above about 30 % vol. The next three gels had yield stresses of < 10, 19, and 154 Pa (< 100, 190, and 1540 dynes/cm$^2$) at total $N_2O_4$ concentrations of 33.7, 40.1, and 45.6 % vol, respectively. These data suggest that gels formed under these conditions and at similar ratios of $N_2O_4$ gelant to $N_2O_4$ particles would become too thick for practical use at total $N_2O_4$ concentrations above about 50 % vol.

The last two gels listed in the lower part of Table X contained $N_2O_4$ particles formed from subcooled $N_2O_4$ and were gelled with $N_2O_4$ gelant formed from a very dilute $N_2O_4$ gas mixture (4.1 % vol in helium). They exhibited yield stresses of 43 and 1470 Pa (430 and 14,700 dynes/cm$^2$) at total $N_2O_4$ concentrations of 59.9 and 67.4 % vol, respectively. These data suggest that gels formed under these conditions and at similar ratios of $N_2O_4$ gelant to $N_2O_4$ particles would be practical to use from the standpoint of yield stress (i.e., stiffness) at total $N_2O_4$ concentrations up to about 65 % vol, a very high solids loading.

# C. SUMMARY OF ACCOMPLISHMENTS

This research clearly demonstrated the ability to produce heterogeneous gels of solid $N_2O_4$ in liquid oxygen free of any other components. The solid $N_2O_4$ was produced in different particle sizes such that it could function as both the gelling agent and as a high-density additive to the liquid oxygen. Various gels of this type were prepared which contained 6.1 to 67.4 % vol (10.1 to 78.1 % wt) of solid $N_2O_4$. These gels exhibited yield stresses ranging from less than 10 to nearly 1500 Pa (< 100 to nearly 15,000 dynes/$cm^2$) and had densities ranging from 1192 to 1726 kg/$m^3$ (74.4 to 107.8 lb/$ft^3$) at 90.18 K (-297.35 °F).

Fine $N_2O_4$ particles were successfully prepared by two approaches. The first involved the subsurface injection of various gaseous mixtures of $N_2O_4$ and helium or $N_2O_4$ and oxygen (3.6 to 55.4 % vol $N_2O_4$) into liquid nitrogen or liquid oxygen using a special vacuum-jacketed, internally heated injection tube  Depending upon the concentration of $N_2O_4$ in the gas mixtures, particle sizes ranged from less than 1 $\mu$m to approximately 200 $\mu$m and particle yields ranged from approximately 55 to 80 % of the injected $N_2O_4$. The second particle preparation approach involved injecting liquid $N_2O_4$ onto the surfaces of liquid nitrogen and liquid oxygen via a single small orifice directed normal to the liquid surface. Particle sizes and yields were dependent upon the condition of the $N_2O_4$ discharged from the injector. Flashing $N_2O_4$ produced particles approximately 4 to 50 $\mu$m in dia. in a yield of about 28 % whereas subcooled $N_2O_4$ produced particles 4 to 360 $\mu$m in dia. in approximately 70 % yields. Particles prepared by the former approach exhibited good gelling capabilities. Particles prepared by the latter approach using flashing $N_2O_4$ and subcooled $N_2O_4$ could be loaded in liquid oxygen to the extent of about 20 to 27 and 55 to 65 % vol, respectively.

Three types of heterogeneous liquid oxygen-solid $N_2O_4$ systems were prepared and evaluated: (1) settled slurries, (2) thick slurries and (3) gels. The settled and thick slurry studies defined the approximate minimum and maximum loadings of $N_2O_4$ that were achievable in liquid oxygen with the various types of $N_2O_4$ particles. Fourteen heterogeneous gels of solid $N_2O_4$ in liquid oxygen were prepared using "$N_2O_4$ gelant". These gels varied in total $N_2O_4$ concentration from 6.1 to 67.4 % vol (10.1 to 78.1 % wt), exhibited yield stresses that varied from < 10 to nearly 1500 Pa (< 100 to nearly 15,000 dynes/$cm^2$), and had densities in the range of 1192 to 1726 kg/$m^3$ (74.4 to 107.8 lb/$ft^3$) at 90.18 K (-297.35 °F). This research clearly demonstrated the feasibility of preparing a new class of dense, high-energy, cryogenic gelled heterogeneous oxidizers and established some of their more important properties.

# VI. CHARACTERIZATION OF HETERGENEOUS GELS

The characterization research performed in this task, Task V, involved three types of evaluations: (1) physical properties (i.e., densities and yield stresses), (2) physical stability, and (3) rheological behavior. These characterizations were performed on the best simple gels prepared under Task III and the best heterogeneous gels prepared under Task IV. The apparatus and/or methods employed in characterizing the gels are described in Section III.C.4. Much of the pertinent test data have been presented in Sections IV and V. In this section, the characteristics of the "best" of the simple liquid oxygen gels and heterogeneous liquid oxygen/$N_2O_4$ gels are presented. The basic characteristics of typical members of this important new class of high-energy-density oxidizers are defined and, thereby, provide a basis for assessing their potential as advanced propellants.

## A. SIMPLE LIQUID OXYGEN GELS

Simple oxygen gels were successfully prepared using both dilute gaseous $N_2O_4$ mixtures and Cab-O-Sil as gelling agents (see Section IV). The characteristics of both of these types of gels are given in the following sections.

### 1. Densities

Depending upon the particular $N_2O_4$-diluent gas mixture used as the gelling agent and the desired stiffness (i.e., yield stress) of the gel, the concentration of $N_2O_4$ present in the gel can vary from a minimum of about 2 % vol (3.4 % wt) to approximately 10 % vol (16.1 % wt). In liquid oxygen/Cab-O-Sil gels, the Cab-O-Sil concentration can vary from about 2 to 3 % vol (3.8 to 5.6 % wt). The densities of gels having these ranges of gelant concentrations are given in Table XI. Densities were derived by the method described in Section III.C.4.e.

### 2. Yield Stresses

The yield stresses of simple liquid oxygen gels prepared with $N_2O_4$-diluent gas mixtures and with Cab-O-Sil are summarized in Figure 17 for various gelant concentrations. From Figure 17, it is evident that Cab-O-Sil is a more effective gelling agent than are the $N_2O_4$-gas mixtures. However, Cab-O-Sil has the disadvantages of (1) greater specific impulse degradation than $N_2O_4$ and (2) it would exist as a solid residue upon evaporation of the oxygen, whereas $N_2O_4$ would readily evaporate. Taking a yield stress value of 100 Pa (1000 dynes/$cm^2$) as typical for a gelled

## Table XI

### Densities of Simple Liquid Oxygen Gels

| Gelling Agent | Concentration of Gelant, | | Density of Gel, [1] | |
|---|---|---|---|---|
| | % vol | % wt | kg/cu m | lb/cu ft |
| N2O4 | 2.0 | 3.4 | 1158 | 72.3 |
| | 4.0 | 6.7 | 1174 | 73.3 |
| | 6.0 | 9.9 | 1191 | 74.3 |
| | 8.0 | 13.1 | 1207 | 75.4 |
| | 10.0 | 16.1 | 1224 | 76.4 |
| | 2.4 | 4.0 | 1161 | 72.5 |
| | 3.6 | 6.0 | 1171 | 73.1 |
| | 4.8 | 8.0 | 1181 | 73.7 |
| | 6.0 | 10.0 | 1191 | 74.4 |
| | 7.3 | 12.0 | 1202 | 75.0 |
| | 8.6 | 14.0 | 1213 | 75.7 |
| | 9.9 | 16.0 | 1223 | 76.4 |
| Cab-O-Sil | 2.0 | 3.8 | 1162 | 72.6 |
| | 2.5 | 4.7 | 1167 | 72.9 |
| | 3.0 | 5.6 | 1173 | 73.2 |
| | 2.1 | 4.0 | 1163 | 72.6 |
| | 2.4 | 4.5 | 1166 | 72.8 |
| | 2.7 | 5.0 | 1169 | 73.0 |
| | 2.9 | 5.5 | 1172 | 73.2 |

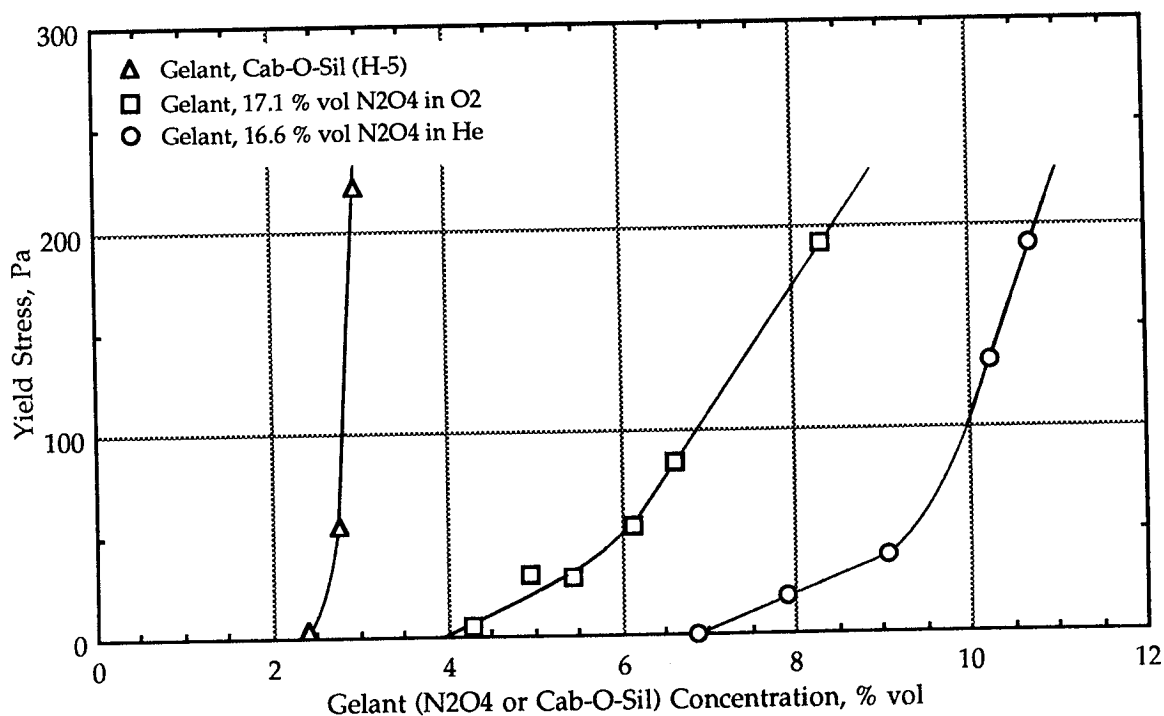[1] Value at the normal boiling point of oxygen, 90.18 K (-297.35 °F)



Figure 17. Yield Stresses of Simple Liquid Oxygen Gels Prepared with Various Gelants

propellant with excellent long-term storability, it can be seen that about 2.8 % vol Cab-O-Sil or 7 to 10 % vol of $N_2O_4$ would be typical gelant concentrations for very stable simple liquid oxygen gels.

## 3. Physical Stability

Observations of simple liquid oxygen/gelant systems defined the concentrations of various gelants necessary to prevent the formation of supernatant layers for short periods (0.5 to 1 hr) at an acceleration of 1 g. Such systems correspond to settled slurries which have very limited physical stability. They can also be considered as "gels" with approximately zero yield stresses. Yield stress measurements were also performed on various simple gels. As mentioned above, typical storable gelled propellants have yield stresses near 100 Pa (1000 dynes/$cm^2$), and are normally physically stable for many years at 1 g or for many minutes at accelerations up to 500 g's. A practical level of physical stability for a cryogenic gel (where long-term storability is not a criterion for use) is probably on the order of 25 Pa (250 dynes/$cm^2$) based on storability work on methane[10], oxygen difluoride[11], and diborane[11] gels. Using yield stresses of zero, 25 and 100 Pa (0, 250, and 1000 dynes/$cm^2$) as criteria for defining gels with minimal, good and excellent physical stabilities, gel compositions corresponding to each of those levels of stability are summarized in Table XII.

### Table XII

### Physical Stabilities and Gelant Concentrations of Simple Liquid Oxygen Gels

| Gelling Agent | Stabilty Level | Gelling Agent Concentration, % vol (% wt) | | |
| --- | --- | --- | --- | --- |
| | | Minimal Stability [1] | Good Stability [2] | Excellent Stablity [3] |
| Cab-O-Sil (H-5) | | ≈ 1.6 (≈ 3.0) | ≈ 2.6 (≈ 4.9) | ≈ 2.8 (≈ 5.3) |
| 17.1 % vol N2O4 in O2 | | ≈ 4 (≈ 6.7) | ≈ 5 (≈ 8.3) | ≈ 7 (≈ 11.5) |
| 16.6 % vol N2O4 in He | | ≈ 7 (≈ 11.5) | ≈ 8 (≈ 13) | ≈ 10 (≈ 16) |

[1] Yield stress ≈ 0 Pa but no supernatant layer at 1 g after 0.5 to 1 hr of storage at 77.35 K
[2] Yield stress ≈ 25 Pa (250 dynes/sq cm)
[3] Yield stress ≈ 100 Pa (1000 dynes/sq cm)

## 4. Rheological Behavior

The rheological characterization of simple gels proved to be more difficult to perform than anticipated with both the Brookfield viscometer and the flow coils. In many cases, the gel viscosities

were greater than the maximum range of the Brookfield viscometer and poor visibility in the integrated preparation and characterization apparatus (Figure 5) generally precluded such measurements.

Some viscosity data were, however, obtained with the Brookfield viscometer on gels prepared with an $N_2O_4$-He gas mixture containing 16.6 % vol $N_2O_4$ and with Cab-O-Sil as gelants. The viscosities of the gels prepared with the $N_2O_4$-He gelant mixture are shown in Figure 11 and for the gels prepared with Cab-O-Sil in Figures 14 and 15. These figures clearly show that viscosities decrease dramatically with gelant concentration for both types of gels at constant shear rates (i.e., rotational speeds, rev/min.) and also with increasing shear rates at constant compositions. This behavior is entirely consistent with that observed in many other particulate gels[5-11].

Two viscosity data points were obtained on a gel prepared in the integrated gel preparation and characterization apparatus using an $N_2O_4$ gas mixture (4.2 % vol $N_2O_4$ in helium) as the gelant. The resulting gel contained approximately 9.6 % vol $N_2O_4$. The viscosity of the gel was 0.25 Pa•s (250 cp) as determined with the Brookfield viscometer at 6 rev/min. This value is about one-half that of the related gel at similar $N_2O_4$ content and shear rate (6 rev/min.) as shown in Figure 11. The viscosity was also determined at 77.35 K (-320.44 °F) by flowing the gel through a 15.2-m (50 ft) coil of copper tubing (4.826 mm, 0.19 in, I.D.) at a flow rate of 33.40 $cm^3$/s (0.5293 gal/min). The corresponding pressure drop and Reynolds number for those flow conditions were 0.2559 MPa (37.12 $lb/in^2$) and 1679, respectively. Since the flow was in the laminar regime, the true viscosity was definable from classical fluid dynamic relationships (see Appendix C). The flow test thus defined the viscosity of the gel to be $6.70 \times 10^{-3}$ Pa•s (6.70 cp or $4.50 \times 10^{-3}$ lbm/ft•s) at a shear rate of 3026 $s^{-1}$ which is approximately 23 times the viscosity of neat liquid oxygen at the same temperature.

## B. HETEROGENEOUS LIQUID OXYGEN GELS

Heterogeneous oxygen gels were successfully prepared using dilute gaseous $N_2O_4$ mixtures as gelling agents (see Section V). The characteristics of those gels are given in the following sections.

### 1. Densities

Depending upon the particular $N_2O_4$-diluent gas mixture used as the gelling agent, the desired yield stress (stiffness) of the gel, and the desired concentration of $N_2O_4$ particles in the gel, the total $N_2O_4$ content can be controlled from about 5 to 65 % vol (8.3 to 76 % wt). The densities of heterogeneous gels having that range of gelant concentrations are given in Table XIII. Densities were derived by the method described in Section III.C.4.e.

## Table XIII

### Densities of Heterogeneous Liquid Oxygen Gels

| TotalConcentration of N2O4, | | | Density of Gel, [1] | |
|---|---|---|---|---|
| % vol | % wt | | kg/cu m | lb/cu ft |
| 5.0 | 8.3 | | 1183 | 73.8 |
| 10.0 | 16.1 | | 1224 | 76.4 |
| 15.0 | 23.4 | | 1266 | 79.0 |
| 20.0 | 30.2 | | 1307 | 81.6 |
| 25.0 | 36.5 | | 1349 | 84.2 |
| 30.0 | 42.5 | | 1390 | 86.8 |
| 35.0 | 48.2 | | 1432 | 89.4 |
| 40.0 | 53.5 | | 1473 | 92.0 |
| 45.0 | 58.6 | | 1515 | 94.6 |
| 50.0 | 63.3 | | 1556 | 97.2 |
| 55.0 | 67.9 | | 1598 | 99.7 |
| 60.0 | 72.2 | | 1639 | 102.3 |
| 65.0 | 76.2 | | 1681 | 104.9 |
| 6.0 | 10 | | 1191 | 74.4 |
| 9.3 | 15 | | 1218 | 76.0 |
| 12.6 | 20 | | 1246 | 77.8 |
| 16.2 | 25 | | 1275 | 79.6 |
| 19.9 | 30 | | 1306 | 81.5 |
| 23.8 | 35 | | 1338 | 83.5 |
| 27.8 | 40 | | 1372 | 85.7 |
| 32.1 | 45 | | 1408 | 87.9 |
| 36.7 | 50 | | 1445 | 90.2 |
| 41.4 | 55 | | 1485 | 92.7 |
| 46.5 | 60 | | 1527 | 95.3 |
| 51.8 | 65 | | 1571 | 98.1 |
| 57.5 | 70 | | 1618 | 101.0 |
| 63.5 | 75 | | 1668 | 104.1 |

[1] Value at the normal boiling point of oxygen, 90.18 K (-297.35 °F)

## 2. Yield Stresses

The yield stresses of three series of heterogeneous liquid oxygen gels prepared with $N_2O_4$ -helium gas mixtures as gelants are summarized in Figure 18 for various total $N_2O_4$ concentrations and fractions of the $N_2O_4$ present as gelant. Particles were formed from flashing $N_2O_4$ in two of the series of gels and from subcooled $N_2O_4$ in the third series. The gels prepared with flashing $N_2O_4$ exhibited given yield stresses at lower total $N_2O_4$ concentrations than the gels prepared using subcooled $N_2O_4$. This behavior is attributed to the fact that flashing $N_2O_4$ produces smaller particles than the subcooled material and these smaller particles contribute to gel structure. The difference in the yield stress/$N_2O_4$ concentration relationships between these two series of gels is believed to be the result of different $N_2O_4$ temperatures (and amounts of flashing ) since other conditions were virtually constant. The data shown in Figure 18 clearly demonstrate that
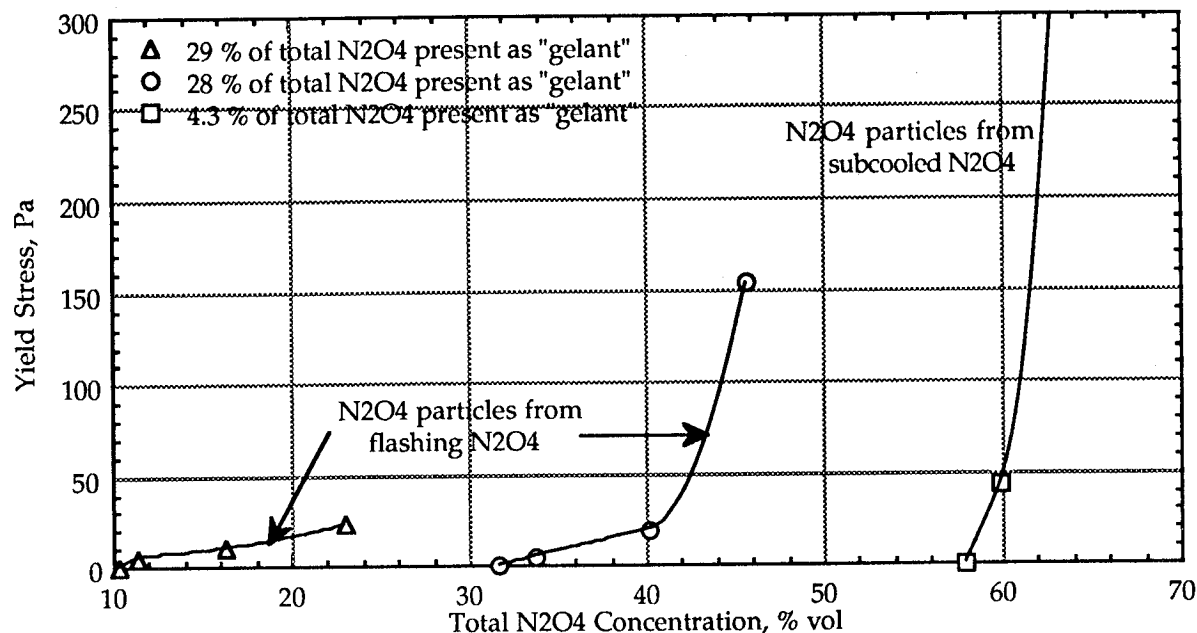
Figure 18. Yield Stresses of Heterogeneous Liquid Oxygen Gels

heterogeneous gels containing up to at least 60 % vol of total $N_2O_4$ can be prepared and the yield stresses of the gels can be controlled over wide ranges.

## 3. Physical Stability

A number of heterogeneous liquid oxygen/gelant systems were observed to define the concentrations of $N_2O_4$ necessary to prevent the formation of supernatant layers for short periods (0.5 to 1 hr) at an acceleration of 1 g (see Table IX). Such systems correspond to settled slurries which have very limited physical stability. They can also be considered as "gels" with approximately zero yield stresses. Yield stress measurements were also performed on various heterogeneous gels (see Table X). As mentioned earlier, typical storable gelled propellants have yield stresses near 100 Pa (1000 dynes/cm$^2$), and are normally physically stable for many years at 1 g or for many minutes at accelerations up to 500 g's. A practical level of physical stability for a cryogenic gel (where long-term storability is not a criterion for use) appears achievable at a yield stress on the order of 25 Pa (250 dynes/cm$^2$) based on previous cryogenic gel work[10,11]. Using yield stresses of zero, 25 and 100 Pa (0, 250, and 1000 dynes/cm$^2$) as criteria for defining gels with minimal, good, and excellent physical stabilities, heterogeneous gel compositions corresponding to each of those levels of stability are summarized in Table XIV.

Table XIV

**Physical Stabilities and Compositions of Heterogeneous Liquid Oxygen Gels**

| Gelling Agent, Conc. of N2O4 in He | Type of N2O4 Used for Part. Preparation | Percent of Total N2O4 as Gelant | Stab. Level | Total N2O4 Concentration, % vol (% wt) [1] | | |
|---|---|---|---|---|---|---|
| | | | | Minimal Stability [2] | Good Stability [3] | Excellent Stablity [4] |
| 4.3 % vol | Flashing | 29 | | 10.3 (16.6) | $\approx$ 24 ($\approx$ 35) | Undefined |
| 17.6 % vol | Flashing | 28 | | 31.6 (44.4) | $\approx$ 41 ($\approx$ 55) | $\approx$ 44 ($\approx$ 58) |
| 4.1 % vol | Subcooled | 4.3 | | 58 (70) | $\approx$ 59 ($\approx$ 71) | $\approx$ 61 ($\approx$ 73) |

[1] Gels are assumed to be at the normal boiling point of oxygen (90.18 K)
[2] Yield stress $\approx$ 0 Pa but no supernatant layer at 1 g after 0.5 to 1 hr of storage at 77.35 K.
[3] Yield stress $\approx$ 25 Pa (250 dynes/sq cm)
[4] Yield stress $\approx$ 100 Pa (1000 dynes/sq cm)

## 4. Rheological Behavior

The rheological characterization of heterogeneous gels was attempted with a Brookfield viscometer. All heterogeneous gels with a yield stress greater than 20 Pa (200 dynes/cm$^2$) exhibited viscosities beyond the upper limit of the instrument ,i.e., > 1.67 Pa•s (> 16.7 poise) at a rotational speed of 6 rev/min. A single definitive viscosity value was obtained on a gel of yield stress 19.4 Pa (194 dynes/cm$^2$) containing a total of 40 % vol N2O4 (28 % of which was "N2O4 gelant"). That specific gel had a viscosity of 0.483 Pa•s (4.83 poise) at a rotational speed of 6 rev/min. This value is roughly twice that of a simple liquid oxygen/Cab-O-Sil gel of similar yield stress (see Figure 15 at a Cab-O-Sil concentration of $\approx$ 2.5 % vol and 6 RPM) and about three times the viscosity of a simple liquid oxygen/N2O4 gel of similar yield stress (see Gel C-9 in Table IV and Figure 11 at 7.89 % vol N2O4). These comparisons suggest that the heterogeneous gels have viscosities 2 to 3 times greater than the simple gels of similar yield stress and at low shear rates.

## VII. SUMMARY

Four types of simple cryogenic gels were prepared and evaluated. Initial effort involved the preparation of liquid nitrogen gels using N2O4 as the gelling agent and a dilute vapor-phase injection method for introducing the gelling agent into the cryogen. The initial work served as a checkout of the test equipment and a first proof-of-principle demonstration that minute N2O4 particles would gel a nonpolar cryogen. Subsequently, two types of liquid oxygen gels were similarly prepared using N2O4 diluted with helium and with gaseous oxygen, respectively, as gelling agents. Liquid oxygen gels containing 3 to 33 % vol (4 to 45 % wt) N2O4 were evaluated in regard to physical stability, structure, and rheological behavior. Liquid oxygen gels were also prepared using Cab-O-Sil (H-5) as the gelling

agent and a simple high-shear mixing technique to disperse it in the liquid oxygen. Liquid oxygen gels containing 1.1-3.4 % vol (1.9-6.0 % wt) Cab-O-Sil (H-5) were evaluated in respect to physical stability, structure, and rheological behavior.

The preparation of heterogeneous gels of solid $N_2O_4$ in liquid oxygen free of any other components was successfully demonstrated. The solid $N_2O_4$ was produced in different particle sizes such that it could function as both the gelling agent and as a high-density additive to the liquid oxygen. Various gels of this type were prepared which contained 6.1 to 67.4 % vol (10.1 to 78.1 % wt) of solid $N_2O_4$. These gels exhibited yield stresses ranging from less than 10 to nearly 1500 Pa (< 100 to nearly 15,000 dynes/cm$^2$) and had densities ranging from 1192 to 1726 kg/m$^3$ (74.4 to 107.8 lb/ft$^3$) at 90.18 K (-297.35 °F).

## VIII. CONCLUSIONS AND RECOMMENDATIONS

This program demonstrated the technical feasibility of the formulation of a new class of high energy-density liquid propellants, namely, the dense cryogenic, gelled, heterogeneous oxidizers. Model gels of this new class of propellants, liquid oxygen/solid nitrogen tetroxide gels, were prepared using two different gelling agents: (1) extremely small particles of solid nitrogen tetroxide and (2) extremely small particles of silica (Cab-O-Sil). Gels containing up to approximately 65% vol (76 % wt) of solid nitrogen tetroxide were formulated. Various gel compositions were characterized in sufficient detail to establish both the technical feasibility of their preparation and the practicality of their use in liquid propulsion systems. These findings strongly indicate that the potential high performance and low environmental impact theoretically attainable by this new class of propellant are achievable without undue research and development.

It is recommended that further development of this promising new class of propellants be pursued at this time. Specifically, the following efforts are recommended as those worthy of most immediate attention:

(1) More detailed characterization of the liquid oxygen/solid nitrogen tetroxide gels in regard to their rheological behavior and aging/storability.

(2) Preparation of a liquid oxygen/solid nitrogen tetroxide gel in sufficient quantity to support demonstration of propellant performance in small-scale thruster test firings.

(3) Perform small-scale thruster test firings to establish delivered performance and handling characteristics.

(4) Extend the investigation of this new high energy-density oxidizers to liquid oxygen/solid hydrogen peroxide gels through initial preparation and

characterization studies. This research would follow the methodology established on this program very closely.

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Appendix A

# DENSITIES OF SOLID NITROGEN TETROXIDE AND LIQUID OXYGEN

## Density of Solid Nitrogen Tetroxide

| Temperature | | Density, | | | Temperature | | Density, | |
| K | °F | kg/cu m | Ref. | | K | °F | kg/cu m | Ref. |
|---|---|---|---|---|---|---|---|---|
| 20.0 | -423.7 | 2013 [a] | 2 | | 222.09 | -59.9 | 1882.4 [b] | 1 |
| 25.0 | -414.7 | 2036 [a, c] | 3 | | 233.0 | -40.3 | 1954 [a, c] | 6 |
| 44.0 | -380.5 | 1994 [a] | 2 | | 234.35 | -37.8 | 1870.1 [b] | 1 |
| 60.0 | -351.7 | 1986 [a] | 2 | | 235.76 | -35.3 | 1868.7 [b] | 1 |
| 78.2 | -319.0 | 1979 | 5 | | 237.25 | -32.6 | 1867.2 [b] | 1 |
| 80.0 | -315.7 | 1975 [a] | 2 | | 245.89 | -17.1 | 1858.6 [b] | 1 |
| 83.2 | -310.0 | 1954 [a, c] | 4 | | 249.40 | -10.7 | 1855.0 [b] | 1 |
| 100.0 | -279.7 | 1966 [a] | 2 | | 255.85 | 0.9 | 1848.6 [b] | 1 |
| 120.0 | -243.7 | 1957 [a] | 2 | | 258.59 | 5.8 | 1845.8 [b] | 1 |
| 140.0 | -207.7 | 1938 [a] | 2 | | 260.0 | 8.3 | 1911 [a, c] | 3 |
| 145.0 | -198.7 | 1989 [a, c] | 3 | | 266.61 | 20.2 | 1837.8 [b] | 1 |
| 194.2 | -110.2 | 1899 | 5 | | | | | |

[a] Calculated from measured crystal lattice dimensions determined from x-ray or neutron diffraction studies.

[b] Calculated at 1 atm. pressure based on multiple linear regression analysis of densities of compressed solid.

[c] Data point not used in data correlation shown in figure below.

[1] Vityuk, L.S., Golovskii, E.A., and Tabachnikov, A.G., "Experimental Study of Thermodynamic Properties of Nitrogen Tetroxide at 230-330 K", Deposited Doc. 1980, SPSLT 39 Khp-D80, Chem. Abstr., 96:92761g(1982)

[2] Kvick, A., et al., J. Chem. Phys., 76(7), 3754-61 (1982)

[3] Cartwright, B.S. and Robertson, J.H., Chem. Commun., 3, 82-3 (1966)

[4] Vegard, L., Nature,126, 916 (1930) and Naturwissenchaften, 18, 1098 (1930)

[5] Biltz, Wilhelm, et al., Z. anorg. allgem Chem., 193, 351-66 (1930)

[6] Broadley, J.S. and Robertson, J.M., Nature, 164, 915, (1949)

$$y = 2017.4 - 0.42747x - 8.9061e\text{-}4x^2 \quad R^2 = 0.999$$

Density of Solid Nitrogen Tetroxide
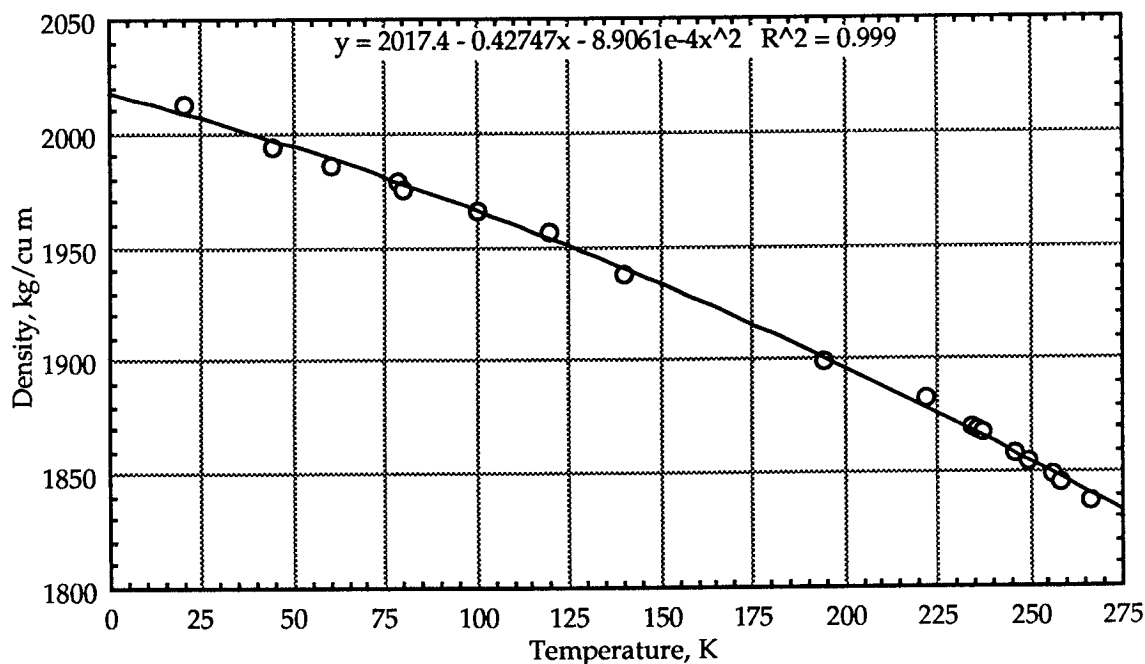
**Density of Saturated Liquid Oxygen [1]**

| Temperature | | Density, | | | Temperature | | Density, | |
|---|---|---|---|---|---|---|---|---|
| K | °F | kg/cu m | lb/cu ft | | K | °F | kg/cu m | lb/cu ft |
| 54.351 | -361.838 | 1306.6 | 81.57 | | 106.0 | -268.9 | 1058.1 | 66.06 |
| 58.0 | -355.3 | 1290.5 | 80.56 | | 110.0 | -261.7 | 1035.4 | 64.64 |
| 62.0 | -348.1 | 1272.8 | 79.46 | | 114.0 | -254.5 | 1011.7 | 63.16 |
| 66.0 | -340.9 | 1254.8 | 78.34 | | 118.0 | -247.3 | 986.9 | 61.61 |
| 70.0 | -333.7 | 1236.7 | 77.21 | | 122.0 | -240.1 | 960.7 | 59.97 |
| 74.0 | -326.5 | 1218.4 | 76.06 | | 126.0 | -232.9 | 932.7 | 58.23 |
| 78.0 | -319.3 | 1199.7 | 74.90 | | 130.0 | -225.7 | 902.8 | 56.36 |
| 82.0 | -312.1 | 1180.8 | 73.72 | | 134.0 | -218.5 | 869.9 | 54.30 |
| 86.0 | -304.9 | 1161.6 | 72.51 | | 138.0 | -211.3 | 833.2 | 52.02 |
| 90.0 | -297.7 | 1141.9 | 71.29 | | 142.0 | -204.1 | 791.4 | 49.41 |
| 90.180 | -297.346 | 1141.0 | 71.23 | | 146.0 | -196.9 | 741.3 | 46.28 |
| 94.0 | -290.5 | 1121.8 | 70.03 | | 150.0 | -189.7 | 675.4 | 42.16 |
| 98.0 | -283.3 | 1101.2 | 68.75 | | 154.0 | -182.5 | 547.3 | 34.17 |
| 102.0 | -276.1 | 1080.0 | 67.42 | | 154.576 | -181.433 | 436.1 | 27.23 |

[1] Roder, H.M. and Weber, L.A., "ASRDI Oxygen Technology Survey. Vol. I, Thermophysical Properties", NASA SP-3071, Nat. Bur. of Stand., Boulder, CO, (1972)



Density of Saturated Liquid Oxygen
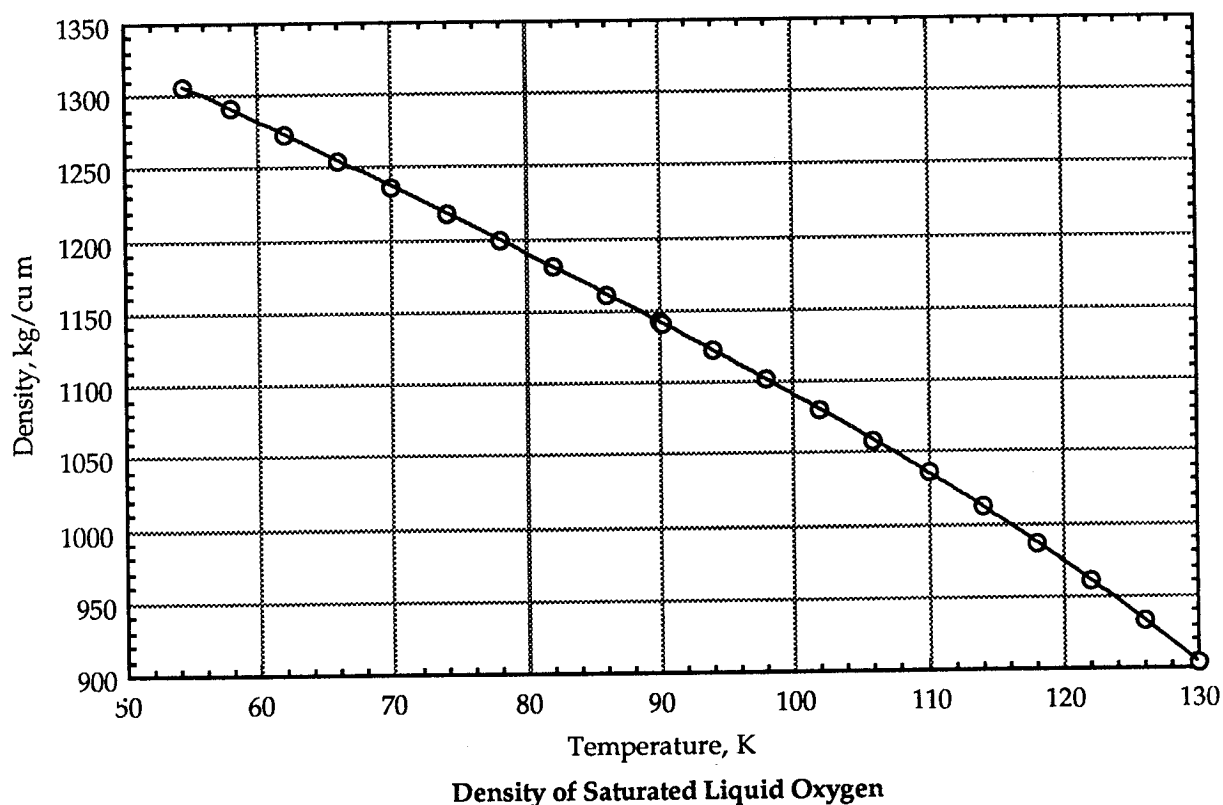
Appendix B

# RELATIONSHIP OF PARTICLE SIZE TO TERMINAL SETTLING VELOCITY

# RELATIONSHIP OF PARTICLE SIZE TO TERMINAL SETTLING VELOCITY

The diameter of a spherical particle is related to its terminal or free-settling velocity, $V_t$, in a surrounding medium by Equation (1):

$$Dp = \frac{3\rho C_d(V_t)^2}{4g(\rho_p - \rho)}$$

(1)

where  $Dp$ = diameter of the particle

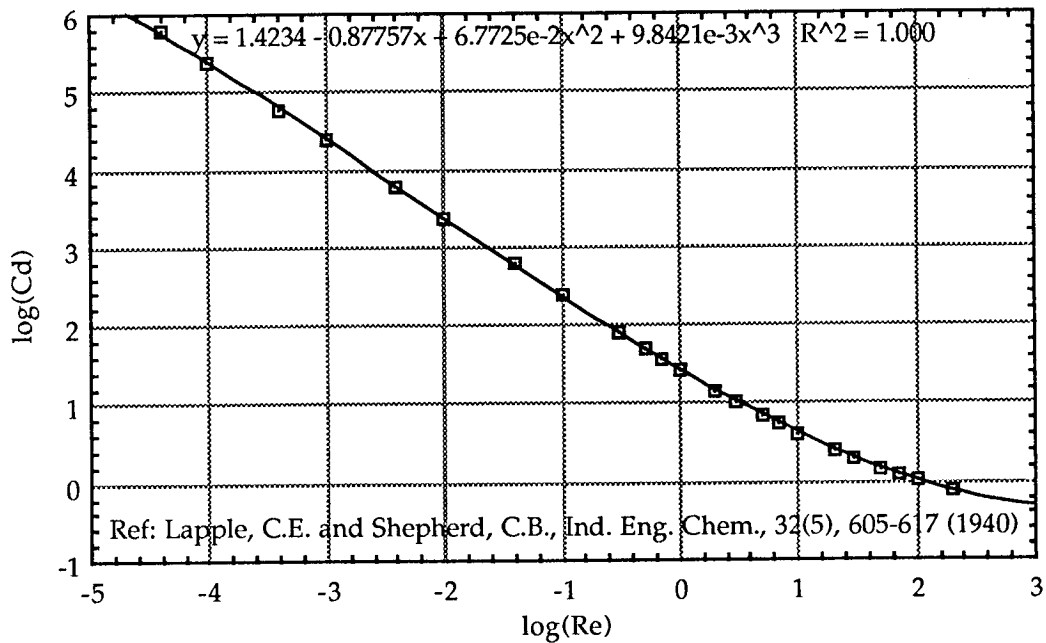$C_d$ = drag coefficient (see figure below)

$g$ = local acceleration of gravity

$V_t$ = free-settling velocity

$\rho_p$ = density of particle

$\rho$ = density of the surrounding medium



$y = 1.4234 - 0.87757x + 6.7725e\text{-}2x^2 + 9.8421e\text{-}3x^3 \quad R^2 = 1.000$

Ref: Lapple, C.E. and Shepherd, C.B., Ind. Eng. Chem., 32(5), 605-617 (1940)

Drag Coefficient as a Function of Particle Reynolds Number

Substituting the appropriate property values for liquid oxygen and solid nitrogen tetroxide at the normal boiling point of nitrogen (77.35 K) into Equation (1) and into the standard expression for the particle Reynolds number, the particle sizes of nitrogen tetroxide corresponding to various free-settling rates in liquid oxygen at 77.35 K were defined by iterative procedures. Using the following property values:

$$\text{Viscosity of } LO_2 \text{ at } 77.35 \text{ K} = 2.8735 \times 10^{-3} \text{ g/cm} \bullet \text{s}$$

$$\text{Density of } LO_2 \text{ at } 77.35 \text{ K} = 1.2028 \text{ g/cm}^3$$

$$\text{Density of } N_2O_4 \text{ at } 77.35 \text{ K} = 1.979 \text{ g/cm}^3$$

the relationships of particle sizes to settling velocities were calculated to be as shown in the following table and figures.

## N2O4 Particle Sizes Calculated from Settling Rates in Liquid Oxygen at the NBP of N2

| Settling Rate, cm/sec | Particle Diameter | | Reynolds Number, Re | Settling Rate, cm/sec | Particle Diameter | | Reynolds Number, Re |
|---|---|---|---|---|---|---|---|
| | cm | μm | | | cm | μm | |
| 0.0001 | 6.24E-05 | 0.624 | 2.61E-06 | 0.35 | 5.04E-03 | 50.39 | 0.7383 |
| 0.0002 | 1.02E-04 | 1.016 | 8.51E-06 | 0.40 | 5.45E-03 | 54.51 | 0.9127 |
| 0.0004 | 1.57E-04 | 1.570 | 2.63E-05 | 0.45 | 5.85E-03 | 58.49 | 1.102 |
| 0.0006 | 1.99E-04 | 1.988 | 4.99E-05 | 0.50 | 6.24E-03 | 62.35 | 1.305 |
| 0.001 | 2.64E-04 | 2.636 | 1.10E-04 | 0.60 | 6.98E-03 | 69.81 | 1.753 |
| 0.002 | 3.78E-04 | 3.784 | 3.17E-04 | 0.70 | 7.70E-03 | 76.99 | 2.256 |
| 0.004 | 5.34E-04 | 5.340 | 8.94E-04 | 0.80 | 8.40E-03 | 83.97 | 2.812 |
| 0.006 | 6.50E-04 | 6.498 | 1.63E-03 | 0.90 | 9.08E-03 | 90.79 | 3.420 |
| 0.01 | 8.30E-04 | 8.297 | 3.47E-03 | 1.00 | 9.75E-03 | 97.5 | 4.081 |
| 0.02 | 1.15E-03 | 11.54 | 9.66E-03 | 1.20 | 1.11E-02 | 110.6 | 5.556 |
| 0.04 | 1.61E-03 | 16.11 | 2.70E-02 | 1.40 | 1.23E-02 | 123.5 | 7.237 |
| 0.06 | 1.97E-03 | 19.67 | 4.94E-02 | 1.60 | 1.36E-02 | 136.2 | 9.123 |
| 0.08 | 2.27E-03 | 22.72 | 7.61E-02 | 1.80 | 1.49E-02 | 148.9 | 11.22 |
| 0.10 | 2.55E-03 | 25.46 | 0.1066 | 2.00 | 1.61E-02 | 161.4 | 13.51 |
| 0.12 | 2.80E-03 | 27.98 | 0.1405 | 2.50 | 1.93E-02 | 192.9 | 20.18 |
| 0.14 | 3.03E-03 | 30.34 | 0.1778 | 3.00 | 2.25E-02 | 224.6 | 28.20 |
| 0.16 | 3.26E-03 | 32.57 | 0.2181 | 3.50 | 2.57E-02 | 256.8 | 37.62 |
| 0.18 | 3.47E-03 | 34.70 | 0.2614 | 4.00 | 2.90E-02 | 289.6 | 48.49 |
| 0.20 | 3.67E-03 | 36.75 | 0.3076 | 4.50 | 3.23E-02 | 323.2 | 60.88 |
| 0.22 | 3.87E-03 | 38.72 | 0.3566 | 5.00 | 3.58E-02 | 357.6 | 74.84 |
| 0.25 | 4.16E-03 | 41.58 | 0.4351 | 5.50 | 3.93E-02 | 392.9 | 90.44 |
| 0.30 | 4.61E-03 | 46.10 | 0.5789 | 6.00 | 4.29E-02 | 429.1 | 107.76 |
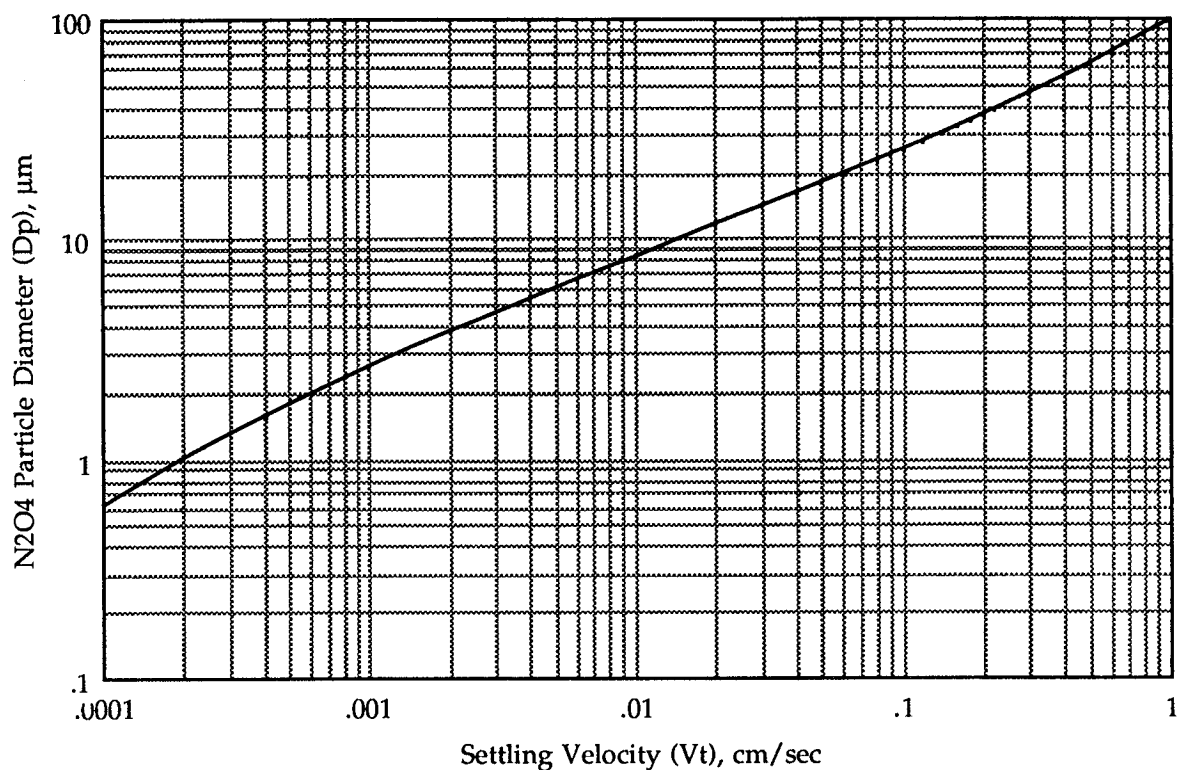
Correlation of N2O4 Particle Diameter with Settling Velocity in LO2 at 77.35 K
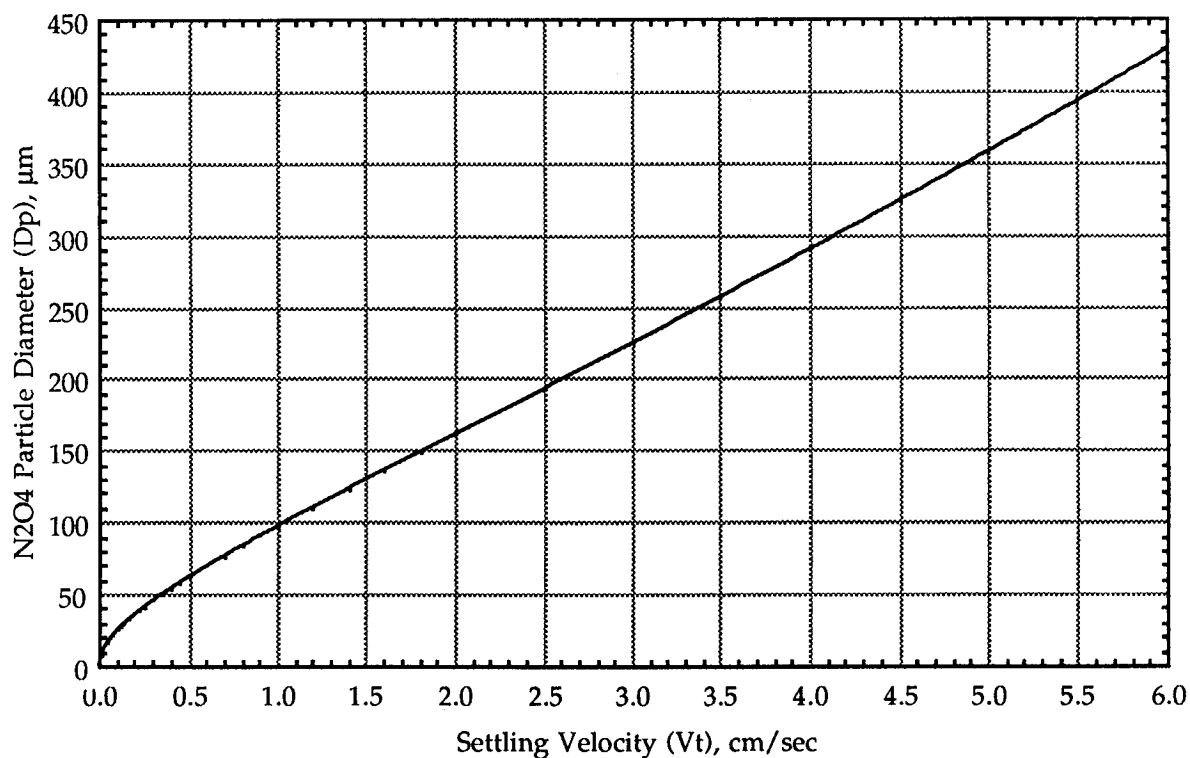


Correlation of N2O4 Particle Diameter with Settling Velocity in LO2 at 77.35 K

Appendix C

# SHEAR STRESS, SHEAR RATE, AND VISCOSITY
# FROM FLOW DATA

# SHEAR STRESS, SHEAR RATE, AND VISCOSITY FROM FLOW DATA

## Shear Stress:

The shear stress on a fluid in laminar flow through a circular passage is related to the length and diameter of the passage and the pressure drop across the length of the duct by Equation (1).

$$\text{Shear Stress (SS)} = \frac{(\Delta P)D}{4L} \tag{1}$$

where $\Delta P$ = pressure drop over the length of the flow passage

$D$ = inside diameter of the flow passage

$L$ = length of the flow passage

## Shear Rate:

The shear rate a fluid experiences in laminar flow in a circular passage is related to the velocity of flow in the passage and diameter of the passage by Equation (2).

$$\text{Shear Rate (SR)} = \frac{8V}{D} \tag{2}$$

where $V$ = velocity of the flow through the passage

$D$ = inside diameter of the flow passage

## Viscosity:

The viscosity is defined as the ratio of shear stress to shear rate as given by Equation (3)

$$\text{Viscosity } (\mu) = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{(\Delta P)D^2}{32LV} \tag{3}$$

## Sample Calculations:

Data: Gel density ($\rho$) at NBP of $N_2$ = 1277 kg/m$^3$ (79.72 lb/ft$^3$); D = 4.826 mm (0.01583 ft); L = 15.24 m (50 ft); V = 1.825 m/s (5.99 ft/sec); and $\Delta P$ = 0.2559 MPa (37.12 lb/in$^2$)

$$\text{Shear Stress (SS)} = \frac{(\Delta P)D}{4L} = \frac{(2.559 \times 10^5 \text{ Pa})(4.826 \times 10^{-3} \text{ m})}{(4)(15.24 \text{ m})} = 20.26 \text{ Pa } (2.939 \times 10^{-3} \text{ lb/in}^2)$$

$$\text{Shear Rate (SR)} = \frac{8V}{D} = \frac{(8)(1.825 \text{ m/s})}{(4.826 \times 10^{-3} \text{ m})} = 3025 \text{ s}^{-1}$$

$$\text{Viscosity } (\mu) = \frac{\text{Shear Stress}}{\text{Shear Rate}} = \frac{(20.26 \text{ Pa})}{(3025 \text{ s}^{-1})} = 6.698 \times 10^{-3} \text{ Pa} \bullet \text{s} \ (4.501 \times 10^{-3} \text{ lb/ft} \bullet \text{sec})$$

$$\text{Reynolds Number (Re)} = \frac{DV\rho}{\mu} = \frac{(4.826 \times 10^{-3} \text{ m})(1.825 \text{ m/s})(1277 \text{ kg/m}^3)}{(6.698 \times 10^{-3} \text{ Pa} \bullet \text{s})} = 1679$$

Since the Reynolds Number is 1679, flow is most likely to be in the laminar regime and the "apparent viscosity" value is a true viscosity.